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by Eugene P. Schoch
Professor of Chemical Engineering
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Second Edition
SECOND IMPRESSION

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GENERAL CHEMISTRY

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PERHAPS THE MOST VALUABLE RESULT OF all education is the ability to make yourself do the thing you have to do, when it ought to be done, whether you like it or not; it is the first lesson that ought to be learned; and however early a man's training begins, it is probably the last lesson that he learns thoroughly.

—*Thomas Henry Huxley*

PREFACE TO THE SECOND EDITION

The first edition of this book, which was written by Professors E. P. Schoch and W. A. Felsing, has been used at The University of Texas over a period of seven years. Early in this period the writer assumed responsibility for the course in which the book has been used, while both Professors Schoch and Felsing assumed other duties. Since the writer and the instructional staff associated with him represented a diversity of training and background different from those of the senior authors of the present volume, it was inevitable that many changes in course content, instructional methods, and viewpoint should accrue. These changes are reflected in the present edition.

When the writer was charged with the task of preparing the second edition, Professors Schoch and Felsing were most generous in that they imposed no restrictions with respect to either the nature or scope of modification of the first edition.

The extent to which the present edition differs from its predecessor will be evident even upon cursory examination. The entire manuscript has been rewritten in a manner that required extensive changes in the order of presentation of much of the subject matter. The laboratory directions have been segregated for inclusion in a separate laboratory manual. While many of the fundamentally sound and desirable features of the first edition have been retained in principle, an effort has been made to present the subject matter from a less specialized viewpoint as well as to expand appropriately the course content. It is hoped that a satisfactory degree of modernization has been achieved without sacrifice of an essentially conservative approach.

The writer takes pleasure in acknowledging his indebtedness to his colleagues, Professors W. A. Felsing, C. S. Garner, and H. R. Henze, for many profitable discussions of educational philosophies and instructional problems. More particularly, thanks are due Professors R. C. Anderson, L. F. Hatch, Norman Hackerman, and Mr. L. K. Yourtee, who gave freely of their time in reading the manuscript and in offering a wealth of constructive criticism and helpful suggestions. The writer wishes also to acknowledge the kindness of Professor Norris W. Rakestraw, editor of *The Journal of Chemical Education*, who supplied a considerable number of the illustrations. The assistance of others who contributed similarly but less extensively is acknowledged elsewhere.

George W. Watt.

Austin, Texas,
September, 1946.

PREFACE TO THE FIRST EDITION

This text, in less complete form, has been in use with freshman chemistry classes at The University of Texas for nearly 30 years. During that time many innovations of presentation and of material have been tested with classes of all sizes; the material contained in this volume is the result of the experience gained.

The text is not written from a descriptive or encyclopedic point of view; in fact, some teachers may complain of the scarcity of such dictionary-like information. Rather, the presentation is based upon chemical principles with just enough descriptive material provided to furnish a basis for generalizations. Thus, after a short introduction to the subject, chemical reactions are presented in two distinct groups: (*a*) those involving no change in valence (or metathetical reactions, and (*b*) those involving a change in valence (or oxidation-reduction reactions). These two classes of reactions involve different fundamentals. Thus, the reactions of the first group depend primarily upon the solubilities and the degrees of activation and of ionization of electrolytes, while the reactions of the second group depend primarily upon the relations between the electromotive forces of half cells. It seems logical, therefore, to present the fundamental principles and facts of each separately.

The text presents, in addition to the inorganic reactions, which constitute the major portion of the book, two chapters on elementary organic reactions. These chapters are largely descriptive and are inserted to aid in the attempt to present a fairly complete picture of the province of chemistry to that student who, by virtue of his selection of a different major, takes only one course in chemistry.

An attempt has been made to enhance the student's interest in the subject by interposing relevant remarks concerning, and descriptions of, industrial applications. The introduction of an abbreviated scheme of qualitative analysis is made partly for the sake of creating interest. Qualitative analysis, if not dwelt upon too long, will heighten the student's interest and help him to get over an otherwise rather prosaic part of the year's work.

The laboratory directions are interspersed with the main portions of the text. This is done because the bearing or the significance of the experimental work should be clearly before the student while he is

doing his laboratory work; this is best accomplished by having the theory and practice appear in juxtaposition in the text. Laboratory exercises have no justification unless they serve to verify the statements made or to clarify with factual material the orderly development of the subject.

This text was written originally to serve only the students at The University of Texas; the authors did not contemplate offering it elsewhere. However, it has been urged upon them that other teachers might be interested in this particular scheme of presentation. Should it prove to be of service to others in the laborious task of teaching the fundamentals of chemistry to college freshmen, the authors will have accomplished their desire.

EUGENE P. SCHOCH.
WILLIAM A. FELSING.

AUSTIN, TEXAS,
May, 1938.

CONTENTS

CHAPTER I
FORMS OF MATTER

The present state of development of the physical and the biological sciences is the result of man's efforts to understand the nature of his environment and its multitude of complex changes. Rapid progress in these specialized fields of knowledge constitutes the single most important factor contributing to the increasing complexity of modern civilization. Consequently, a knowledge, or at least an appreciation, of these fields of human endeavor is an essential possession of any intelligent member of modern society. The course of study outlined in this book is an effort at the presentation of certain fundamental aspects of the science of chemistry, its methods, accomplishments, and aims.

Among the experimental sciences, chemistry and physics occupy a unique position. Their sphere of influence embraces all of the other physical sciences and exerts far-reaching influence upon the biological and even the social sciences. The steadily increasing importance of a knowledge of chemistry has prompted medical educators to require greater and greater emphasis upon the study of this subject in pre-medical curricula as well as in medical schools. Much the same situation prevails with regard to pharmacy, biology, bacteriology, etc. In different degrees, the various phases of engineering, geology, agriculture, etc., present problems which can be solved to best advantage on the basis of at least a limited knowledge of chemistry.

1.1. Nature and Scope of the Science of Chemistry

Chemistry is that branch of the physical sciences which is concerned with the composition of matter and with those transformations which matter undergoes. All objects in the material universe are suitable subjects upon which the interests of the chemist may be focused. Chemistry deals also with energy, since transformations of matter are accompanied by energy changes.

Largely as a matter of convenience, chemistry has come to be thought of as being made up of certain branches or subdivisions. It must be recognized, however, that this sort of classification is quite arbitrary and somewhat artificial. *Inorganic chemistry* is concerned

with substances that have their origin in or are commonly associated with the mineral world, *e.g.*, rocks, ores, the soil, the constituents of the atmosphere, etc. *Organic chemistry* is usually defined as the chemistry of substances that contain carbon, but this designation is not an altogether satisfactory one. *Analytical chemistry* deals with the methods by means of which the chemist can determine the composition of the various forms of matter, whether inorganic or organic. *Physical chemistry* is concerned with the various principles, laws, and theories that enable the chemist to interpret and explain the results of experiments and observations. By virtue of the very nature of its subject matter, physical chemistry becomes an essential part of each of the other branches of chemistry. Each of the four branches referred to above may be and frequently is subdivided further, but since all of these arbitrary subdivisions overlap one another and are so interdependent, it is preferable that the science of chemistry be thought of as a composite whole.

1.2. The Method of Science

It must be recognized at the outset that chemistry is based upon *experiment.* In solving the many problems with which the chemist is faced, a fairly well-defined plan of attack is usually followed. The first step involves experimentation in the laboratory and the systematic recording of observations and experimental data. Following this collecting of information, the chemist must organize the results of his experiments and examine them with a view to discovering any general relationships, principles, or laws in terms of which the observed phenomena may be described. Next, an effort is made to devise suitable theories by means of which the observed facts may be explained satisfactorily. Finally, these theories are applied in the prediction of the behavior of substances not previously studied. Here the objective is the expansion of knowledge and substantiation or disproof of the validity of theories. Such theories are of value not only because they serve in the explanation and understanding of known facts but also because theories frequently suggest lines of investigation that lead to the discovery of new truths.

1.3. Classification of Matter According to Physical State

Because the science of chemistry is concerned with matter in all of its multitude of different forms, simplification for purposes of study requires that every effort be made to organize and classify the materials involved. Initial efforts at classification may achieve only a gross segregation of matter into broad types, each of which upon further

study may have to be divided further into numerous subtypes. Two very broad classifications are indicated in the following paragraphs.

Everyone is aware of the fact that water, which is ordinarily a liquid, may also exist in the form of a gas (steam) or as a solid (ice). Since many other substances are capable of existing in all three of these states of aggregation and since all known forms of matter exist in at least one, it becomes convenient to classify matter according to the three physical states, *viz.*, *solid*, *liquid*, and *gas*. The characteristics of matter as it exists in these conditions will be considered elsewhere in this and in subsequent chapters.

1.4. Classification of Matter According to Composition

A somewhat more involved but nevertheless useful classification of matter may be made in terms of composition. Any object may be classified under one of the three headings: *element*, *compound*, or *mixture*. This classification is by no means so simple as that based on physical state. This fact becomes apparent when one realizes that matter in all the physical states is encountered in each of the three groupings according to composition. Because all the materials encountered in the study of chemistry are classified (according to composition) as elements, compounds, and mixtures, it is essential that the characteristics of each and the distinctions among the three be understood thoroughly. Consequently, each will be considered in some detail.

The student who would learn of chemistry must appreciate the fact that the study of a science involves, in some measure, the same tasks as are encountered in the study of a language. One cannot hope to read, write, or speak a foreign language without first acquiring an adequate vocabulary; neither can one progress in the study of a science without learning the vocabulary that permits one to speak fluently and think in terms of the language of that particular science. From the beginning, therefore, the student should pay particular attention to the exact meaning of terms employed and to distinctions between related terms.

1.5. Elements

Suppose that a sample of ordinary table salt is studied in the laboratory with a view to breaking the salt down into its constituent parts. It will be found by experiment that the white solid salt may be decomposed into two simpler substances. One of the products of this decomposition is a greenish-yellow gas known as *chlorine;* the other is a soft metallic solid known as *sodium.* The object of the experiment has

been realized since it has been demonstrated that table salt is composed of two simple substances. Further experiments must now be performed to determine whether the sodium, the chlorine, or both may be decomposed still further. It will be found that such is not possible by any ordinary means. Another approach to this problem lies in the chance that, even though it is not possible to decompose sodium or chlorine, one might hope to produce sodium or chlorine by bringing together other materials of a more elementary character. Here again, all efforts would be met by failure. The inescapable conclusion, therefore, is that sodium and chlorine must be of elemental nature, *i.e.*, they must be substances that should be classified as elements. **An element is a substance that cannot by any ordinary means be built up from or decomposed into simpler substances.**

The Number and Kinds of Elements. At the middle of the eighteenth century only about 17 elements were definitely known, but by 1890 the number was increased to about 70. At present the identity of 90 elements is firmly established and claims to the discovery of a few more have been made. The question as to the maximum possible number of elements has been the object of much speculation.

Elements may be classed, roughly, into two groups: *metals* and *nonmetals*. The nonmetals constitute more than one-half of the total weight of the earth's crust and include such substances as oxygen, sulfur, carbon, nitrogen, and chlorine. Among the metals found in the earth's crust are such common materials as iron, lead, zinc, copper, aluminum, silver, and gold. Only about one-half of the known elements are usually encountered by the chemist in his work; only rarely does he see or work with the others. The earth's crust together with the sea and the atmosphere is composed largely of 12 elements: oxygen, silicon, aluminum, iron, calcium, magnesium, sodium, potassium, hydrogen, titanium, carbon, and chlorine. Of these, oxygen is by far the most abundant.

1.6. Properties of Substances

If one should be asked to identify two automobiles made by different manufacturers, the distinction between the two could probably be made readily in terms of gross differences in appearance. However, if it became necessary to identify two different makes of automobile produced by the same manufacturer, these two might be so similar that a more careful examination would be required. In any event, there could be found at least enough minor differences to distinguish the one from the other. This same type of problem is involved in the study of chemistry. One of the first tasks that face the student is that

of recognizing certain chemical substances. Each substance has certain characteristics which are usually called *properties.* Thus, ordinary window glass has certain well-defined properties such as hardness, transparency, and ease of fracture. Sulfur is an element having self-evident properties such as color, odor, and taste. **The properties of a substance are those attributes or characteristics in terms of which that substance may be recognized or identified.**

1.7. Compounds

The elements sulfur and lead have properties by which they may be recognized without difficulty. If lead and sulfur are heated together, there is produced a new substance having properties that are very different from those of lead or sulfur. The product of this chemical union is known as *lead sulfide* and is a *compound* containing the elements lead and sulfur. The following conclusions may be drawn from this simple experiment: (1) the union of two simple substances (elements) resulted in the formation of a more complex substance (a compound); (2) upon entering into chemical union the characteristic properties of the two elements disappeared and a new substance having its own set of characteristic properties was produced. On the basis of this and other similar experiments it is possible to arrive at a satisfactory definition of the term *compound.* **A compound is a substance formed from two or more elements. The properties of a compound are different from those of its constituent elements.**

Synthesis and Analysis. The process of producing more complex substances by the union of two or more simple substances is known as *synthesis.* Thus, the synthesis of lead sulfide is accomplished by the union of lead and sulfur. Similarly, the compound known as *water* may be synthesized by the combination of the elements hydrogen and oxygen. The use of the term synthesis is not restricted to the cases involving the union of elements but is also applied commonly, for example, to situations in which two or more compounds unite to form another more complex compound.

The laboratory examination of a substance for the purpose of determining its composition is termed an *analysis.* When a sample of an ore, for example, is sent to a chemical laboratory for analysis, the sender wishes the chemist to examine it for the purpose of finding out what it contains. If the analysis is made only for the purpose of determining the identity of the substances involved, the analysis is said to be *qualitative.* Thus a qualitative analysis of an iron ore might show that the ore consists of iron and oxygen. The analysis might, however, be so conducted as to yield information as to the quantities

of iron and oxygen present in the ore; such an analysis is termed a *quantitative analysis* and might supply the information (for example) that the ore contains 69.9 per cent of iron and 30.1 per cent of oxygen.

1.8. Law of Definite Proportions

The simple fact that a chemical compound consists of two or more elements provides no information as to the quantities of the elements concerned. Suppose that samples of table salt, which is a compound known as *sodium chloride*, are obtained from various parts of the world and purified in order to make certain that every sample is entirely free of impurities. If one of these samples, weighing 1 lb., is subjected to a quantitative chemical analysis, it will be found that the 1 lb. of sodium chloride consists of 0.3934 lb. of sodium and 0.6066 lb. of chlorine. The analysis of another sample of pure sodium chloride from an entirely different source would lead to exactly the same result. Finally, after all the samples are analyzed, it is found that the results are identical, or as nearly so as the accuracy of the experimental method permits. After similar experiments using a wide variety of pure compounds, the conclusions drawn from this experience may be summarized in an expression known as the *law of definite proportions* or sometimes as the *law of constant composition:* **The composition of a pure compound is always precisely the same.**

1.9. Physical and Chemical Changes

The transformations of matter referred to in the preceding paragraphs fall into two distinct classes. The melting of solid ice and the formation of ice from liquid water are examples of *physical change.* It is a well-known fact that a bar of steel may be magnetized and may thereafter behave as a magnet for an indefinite period of time. This also is an example of a physical change. It is of importance to recognize that the chemical composition of the bar of steel was not altered in the process of magnetization; neither did any change in composition result from the transformation of solid water to liquid water. **A physical change may be defined as a transformation of matter which may be accomplished without change in chemical composition.**

The physical changes that occur when heat is applied to ice may be represented as follows:

$$\text{Ice}_{(\text{solid})} \longrightarrow \text{water}_{(\text{liquid})} \longrightarrow \text{steam}_{(\text{gaseous})}$$

Although most solids, when heated, melt to liquids which upon further application of heat are converted to gases, the student should not infer

that this sequence of changes of state will occur in all cases. When solid iodine, for example, is heated, the solid is changed directly to the gas.

$$\text{Iodine}_{(\text{solid})} \rightarrow \text{iodine}_{(\text{gaseous})}$$

That is, the iodine is converted to the gaseous state without first melting to a liquid. This may be demonstrated readily with the simple apparatus shown in Fig. 1. Solid iodine is placed in the bottom of the beaker and a porcelain dish filled with ice water is placed over the top of the beaker. Upon application of heat to the bottom of the beaker, purple gaseous iodine will appear in the space above the solid iodine. When these vapors strike the cold undersurface of the dish, the gaseous iodine condenses to solid crystalline iodine. Such change in which a solid is converted directly to the vapor state followed by direct condensation of the vapor to the solid state is known as *sublimation*. Common physical changes together with descriptive terms employed in speaking of these changes are summarized in Table 1.

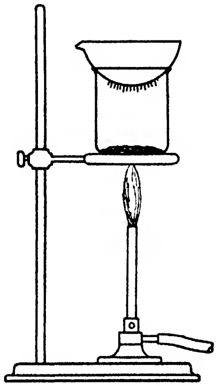

FIG. 1.—Sublimation of iodine.

The decomposition of table salt has been referred to previously. Another change which may be effected easily is the decomposition of ordinary cane sugar. If white crystals of sugar are heated, the sugar

TABLE 1

CHANGES IN STATE

Changes	Descriptive Terms
Solid to liquid	Melting (fusion)
Liquid to gas	Boiling (vaporization, volatilization, evaporation)
Gas to liquid	Liquefaction (condensation)
Liquid to solid	Freezing (solidification)
Solid to gas	Evaporation
Solid to gas to solid	Sublimation

caramelizes and upon further heating decomposes into carbon and water. Both of these transformations appear to involve much more deep-seated changes than were encountered in simple physical changes. Both the table salt and the sugar have been destroyed as such and have been replaced by substances of different properties and different chemical composition. A similar situation was encountered as the result of the formation of lead sulfide by the union of lead and sulfur.

Changes in which one or more substances unite, or are decomposed, to form one or more substances having new properties are called ***chemical changes,*** **or** ***chemical reactions.*** A chemical change is always accompanied by an energy change.

1.10. Law of Indestructibility of Matter

By taking advantage of the possibility of determining the *weights* of materials that undergo physical or chemical change, it becomes possible to arrive at a generalization of fundamental importance. Suppose that a sample of ice weighing exactly 1 lb. is melted under such conditions that none of the resulting liquid water will be lost. If the water formed is weighed accurately, it will be found that from exactly 1 lb. of ice there was produced exactly 1 lb. of water. By an extension of this experiment it could be proved that from 1 lb. of water there may be produced 1 lb. of steam. It now becomes of interest to inquire as to whether a similar result will be obtained from the study of a chemical change.

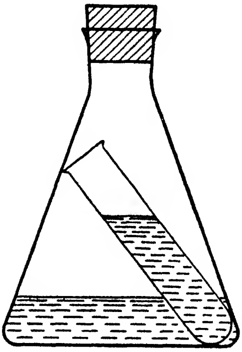

FIG. 2.—Simple demonstration of the law of indestructibility of matter.

The answer to this question may be found by a very simple experiment. Into a flask (Fig. 2) containing a solution of a compound known as *potassium chromate,* there is placed a test tube containing a solution of another chemical compound called *lead nitrate.* The top of the test tube rests against the upper wall of the flask so that the two solutions are not mixed. The flask is then fitted with a tight rubber stopper and the entire assembly weighed accurately. When, without removing the stopper, the flask is inverted so that the two solutions are mixed, there occurs a chemical change in which yellow solid lead chromate is produced. For present purposes, this change may be represented as follows:

$$\underset{\text{(dissolved)}}{\text{Potassium chromate}} + \underset{\text{(dissolved)}}{\text{lead nitrate}} \rightarrow \underset{\text{(solid)}}{\text{lead chromate}} + \underset{\text{(dissolved)}}{\text{potassium nitrate}}$$

If the weight of the flask and its contents is now determined with accuracy, it will be found that the weight is exactly the same as it was before the occurrence of the chemical reaction.

From the experiments described above as well as from many others, it is apparent that matter is neither destroyed nor created as the result

of physical and chemical change. This fact is the basis of the law of indestructibility of matter which may be stated as follows: **The occurrence of physical and chemical changes does not result in any change in the total weight of the materials involved.**

1.11. Mixtures

When two substances are brought together, they do not necessarily combine to form a compound. For example, if iron filings and lumps of sulfur are mixed at ordinary temperatures, chemical combination does not occur. Such a mixture is said to be *heterogeneous* since the component parts of the mixture may be distinguished by the unaided eye. Obviously, it would be possible to separate the components of this mixture merely by picking out the iron filings with a pair of forceps. If, however, this mixture is ground to a very fine powder, the two components become so intimately mixed that the individual particles can no longer be recognized. Under these conditions, the mixture is said to be *homogeneous.*[1] If a horseshoè magnet is drawn through this homogeneous mixture, the powdered iron is attracted and held by the magnet while the particles of sulfur are not. Thus, the iron and sulfur may be separated by repeated use of the magnet. It may be concluded that the components of a mixture may be separated by purely mechanical means.

Distinction between Mixtures and Compounds. If a homogeneous or heterogeneous mixture of iron and sulfur is heated, they unite to form a compound known as *iron sulfide.* The component parts of this or any other compound may not be separated by the use of forceps, magnets, or any other purely mechanical methods. Only by decomposition which involves chemical change may the lead and sulfur be separated and recovered in their original forms. Consequently, the mixtures and compounds differ in that mixtures may be separated into their component parts by mechanical means whereas a compound may be separated into its constituents only by the use of chemical methods.

1.12. Atomic Theory

Having recognized that the chemical elements represent relatively simple units of matter, one is led to inquire into the exact nature of

[1] Care must be exercised to make clear the basis for the use of this term. A mixture that appears homogeneous to the unaided eye may be quite evidently heterogeneous when viewed under a microscope. Unless otherwise indicated, the use of the term *homogeneous* in this book implies homogeneity as judged by the unaided eye.

these elemental substances. Historically, the concept that all matter is composed of small discrete particles dates back to the Greek philosophers who lived several centuries before Christ. Their ideas were not based upon any experimental evidence since they believed experimentation to be beneath their dignity. Nevertheless, these ideas as to the particulate character of matter persisted down through the centuries even without any quantitative experimental basis. In 1804, the English chemist, John Dalton (Fig. 3), in an effort to explain such fundamental laws as the law of indestructibility of matter and the law of definite proportions, revived and extended these concepts to the extent of presenting a rather complete picture as to how he believed chemical combination occurred. This theory, which has come to be known as *Dalton's atomic theory*, embraced many erroneous ideas which have long since been discarded. The essential and useful features of this atomic theory in a somewhat modified form may be summarized as follows:

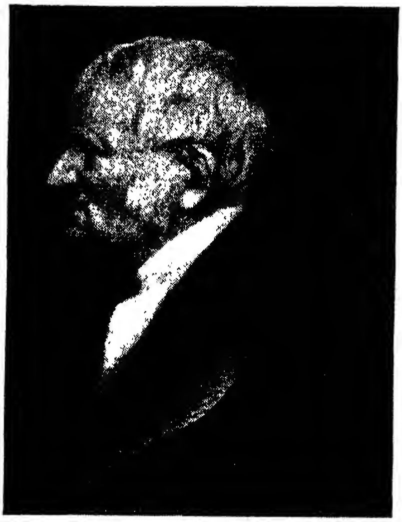

Fig. 3.—John Dalton (1766–1844).

1. Each element is made up of small particles called *atoms*.
2. The atoms of a given element have the same weight and are identical in every respect.
3. Atoms of different elements are dissimilar and have different weights.
4. During chemical or physical change, atoms are not subdivided.
5. Atoms have the ability to attract other like or unlike atoms and to hold them in chemical combination.
6. Two or more atoms unite to form particles known as *molecules*.
7. Atoms combine in simple whole-number ratios, and for any pure substance the ratio is always the same.
8. Atoms of two different elements may combine in more than one ratio to form different compounds.

In Dalton's time so little was known about the relative weights of the atoms of the different elements that the theory failed to receive the recognition that it merited. The true value of Dalton's views did not become apparent until 1860 when the Italian chemist, Cannizzaro

(Fig. 4), suggested a clear procedure by means of which numerical values for the relative weights of atoms might be assigned. At the present time, although scientists are fully cognizant of the significance of Dalton's early work, it must be recognized that modern knowledge requires that the theory as outlined above must be accepted only after certain further modifications. Several such modifications will become apparent or will be pointed out in later chapters.

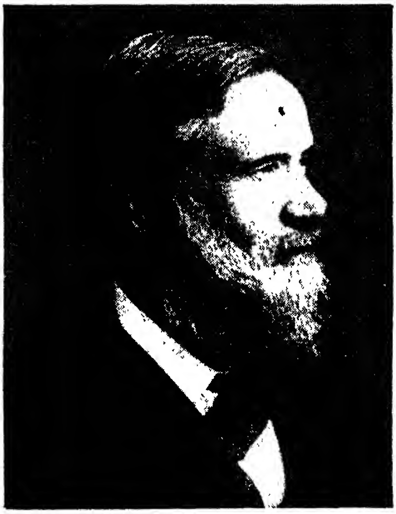

FIG. 4.—Stanislao Cannizzaro (1826–1910).

Atoms and Molecules. In the light of Dalton's theory, **an atom may be defined as the smallest particle of an element capable of taking part in a chemical reaction.** If unlike atoms unite, molecules of a compound are produced. For example, atoms of the element hydrogen combine with atoms of the element oxygen and form molecules of the compound known as *water*. The union of two or more atoms of the same kind, however, results in the formation of molecules of the element concerned. Thus, 2 atoms of the element oxygen unite to form a molecule of the element oxygen. The molecules of most of the elemental gases such as oxygen, hydrogen, nitrogen, and chlorine contain 2 atoms under ordinary conditions. The molecule of the element sulfur may contain 2, 4, 6, or 8 atoms; that of phosphorus usually 4, arsenic 4, etc. **A molecule is defined as the smallest unit of matter capable of a separate distinct physical existence.** On the basis of this none too satisfactory definition, the terms *atom* and *molecule* in some cases are synonymous. The atoms of the inert gases of the atmosphere (helium, neon, argon, krypton, and xenon) do not combine to form molecules. Accordingly, the atom of helium is the smallest particle of helium capable of a separate physical existence and hence qualifies under the above definition of a molecule. Similarly, most of the metals are usually considered as elements which consist of single atoms rather than molecules containing two or more atoms.

EXERCISES

1. Define the following terms: (*a*) element, (*b*) compound, (*c*) sublimation, (*d*) atom, (*e*) molecule.

2. Distinguish between the following terms: (*a*) compound and mixture, (*b*) synthesis and analysis, (*c*) qualitative and quantitative analysis, (*d*) chemical and physical change, (*e*) homogeneous and heterogeneous mixtures, (*f*) molecules of an element and molecules of a compound.

3. State the law of indestructibility of matter.

4. State the law of definite proportions.

5. Cite two bases upon which matter may be classified.

6. Outline the essential features of Dalton's atomic theory.

7. Explain what is meant by the properties of a chemical substance.

SUGGESTED READING[1]

Journal of Chemical Education

HORN, Relation of Chemistry to Health and Disease, 4, 711 (1927).

HASKINS, The Relation of Chemistry to Agriculture, 4, 723 (1927).

GREENHILL, The Relation of Chemistry to the Development of the Cotton Industry, 4, 743 (1927).

RUTENBER, The Relation of Chemistry to National Defense, 4, 736 (1927).

BARNSLEY, The Relation of Chemistry to the Home, 4, 730 (1927).

ABEL, Chemistry in Relation to Medicine, 6, 1045 (1929).

URBAN, The Relation of Chemistry to the Development of the Petroleum Industry, 3, 683 (1926).

MENSCHUTKIN, Historical Development of the Concept of Chemical Elements, **14**, 59 (1937).

ROBERTSON, Sublimation, 9, 1713 (1932).

DAVEY, The Reality of the Atom, 4, 327 (1927).

FRENCH, The Law of Definite Proportions, 6, 1542 (1929).

DEMING, The Laws of Definite Composition and Definite Proportions, **19**, 336 (1942).

COWARD, John Dalton (1766–1844), 4, 23 (1927).

PARRAVANO, Cannizzaro and the Atomic Theory, 4, 836 (1927).

ATKINSON, The Atomic Hypothesis of William Higgins, **17**, 3 (1940).

[1] Following the name of each chemical journal to which reference is made, there is given the name of the author or authors, the title of the article, the journal volume number, page number, and year of publication. References to books include the name of the author, the title of the book, the name and address of the publisher, and the year of publication.

CHAPTER II

WEIGHT RELATIONSHIPS

Any real appreciation of the nature of chemical change can come only from a knowledge of the *quantities* of the various forms of matter involved. The law of indestructibility of matter could not have been established as a valid generalization had not the French chemist, Lavoisier (Fig. 5), devised a sensitive balance and through its use proved that matter is neither created nor destroyed when chemical

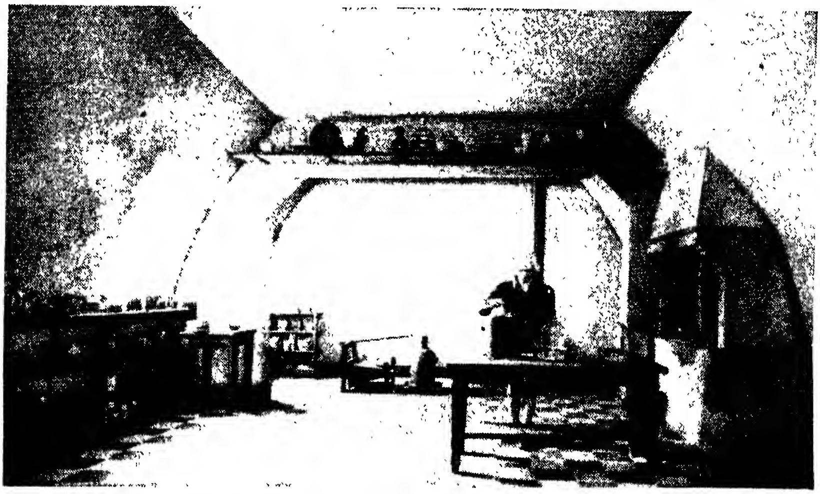

FIG. 5.—Antoine Laurent Lavoisier (1743–1794) in his laboratory.

changes occur. Although done with equipment that was crude by comparison with that in common use at present (Fig. 6), Lavoisier's work represented the beginning of a new era. When chemists learned to study chemical reactions in terms of quantities, chemistry passed from the realm of the arts into the category of the sciences.

2.1. Measurement of Weight

With but few exceptions, the chemist expresses weight in terms of grams or fractions or multiples thereof. This unit of weight, the *gram*, is the weight of a definite volume (1 ml., see Sec. 5.5) of water at a

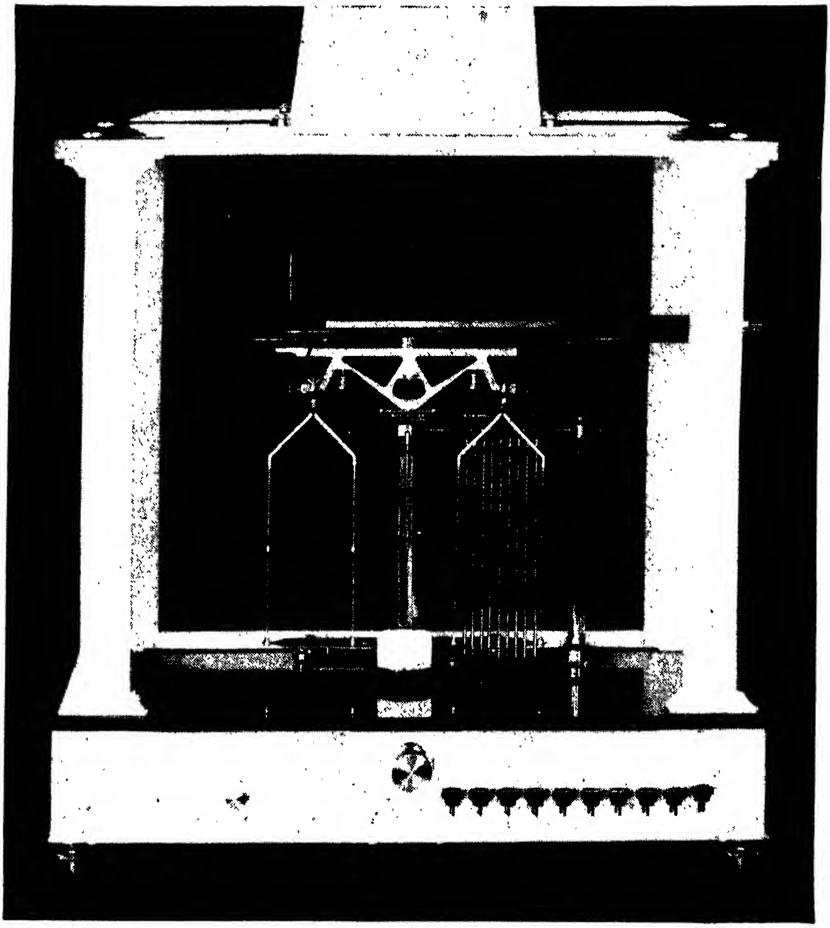

FIG. 6.—A modern chemical balance. (*Courtesy of Wm. Ainsworth and Sons, Inc.*)

temperature of 4° on the centigrade scale.[1] The units most frequently used in chemical work are listed in Table 2; the relation between grams and pounds is included for comparison.

TABLE 2

UNITS USED IN THE MEASUREMENT OF WEIGHT

Unit	Designation
1 gram	Weight of 1 milliliter of water at 4°C.
1 milligram	One one-thousandth of 1 gram (0.001 g.)
1 kilogram	1,000 grams
1 pound	453.59 grams

[1] This temperature scale is different from the Fahrenheit temperature scale used in the home. For an explanation of the centigrade scale and a comparison of these scales, see Sec. 4.11.

The term *gram* is commonly abbreviated by the letter g., which unfortunately is used also by the pharmacist as an abbreviation for another unit of weight, the grain. Similarly, the abbreviations mg. and kg. are used for milligram and kilogram, respectively.

2.2. Law of Multiple Proportions

It has been pointed out in the preceding chapter that, according to the law of definite porportions, the elements that make up any pure chemical compound are always present in exactly the same proportions by weight. A quantitative analysis of water, for example, would show that pure water always consists of 8 parts by weight (grams) of oxygen and 1.008 parts by weight (grams) of hydrogen. As early as the beginning of the nineteenth century, however, chemists were aware of the fact that two given elements may unite to form more than one compound. Thus, the elements nitrogen and oxygen combine to form compounds that are representative of the class of chemical substances known as *oxides*. These oxides are listed in the accompanying table, together with their percentage composition as determined experimentally by quantitative chemical analysis.

Oxide	Oxygen, %	Nitrogen, %
Nitrous oxide	36.35	63.65
Nitric oxide	53.32	46.68
Nitrogen dioxide	69.55	30.45

This information, as such, reveals no apparent relationship among the three compounds. Suppose, however, that it is desired to know how much nitrogen is combined with exactly 1 g. of oxygen in each of these compounds. This information may be had by a calculation involving simple proportion.

Let x = weight of nitrogen combined with 1 g. of oxygen in nitrous oxide.

Then

$$x:1::63.65:36.35$$

$$36.35x = 63.65$$

$$x = \frac{63.65}{36.35}$$

$$x = 1.751$$

Similarly, for each of the three compounds, the weight of nitrogen combined with 1 g. of oxygen may be calculated from the values for the percentage composition.

Oxide	Oxygen, g.	Nitrogen, g.
Nitrous oxide	1	1.751
Nitric oxide	1	0.8755
Nitrogen dioxide	1	0.4378

Now, a very definite relationship becomes apparent. The weights of nitrogen listed above are seen to be simple whole-number multiples of the smallest weight of nitrogen found in combination with 1 g. of oxygen in any of the three compounds,

$$0.4378 = 1 \times 0.4378$$
$$0.8755 = 2 \times 0.4378$$
$$1.751 = 4 \times 0.4378$$

It is by no means accidental that this relationship is found. The same relationship appears in all cases in which two elements combine to form more than one compound. To consider another example, the element chromium is known to form three compounds with oxygen which have the percentage compositions listed in the accompanying table.

Oxide	Oxygen, %	Chromium, %
Chromium monoxide	23.52	76.48
Chromic oxide	31.57	68.43
Chromium trioxide	47.99	52.01

If from these data one calculates (just as before) the weight of chromium combined with 1 g. of oxygen in each of the three compounds, the following results are obtained:

Oxide	Oxygen, g.	Chromium, g.
Chromium monoxide	1	3.252
Chromic oxide	1	2.168
Chromium trioxide	1	1.084

The weights of chromium which, in three different compounds, are combined with 1 g. of oxygen are related as follows:

$$1.084 = 1 \times 1.084$$
$$2.168 = 2 \times 1.084$$
$$3.252 = 3 \times 1.084$$

Such results as obtained in the foregoing examples led Dalton to formulate the law of multiple proportions which may be stated as follows: **When two elements A and B unite to form more than one compound, the weights of B which combine with a fixed weight of A stand to each other in the ratio of small whole numbers.** After a consideration of certain other factors that enter into the picture, it will be seen that the weight relationships that led to the establishment of the law of multiple proportions also serve as a basis for the determination of the relative weights of the various atoms.

2.3. The Standard for Relative Atomic Weights

On the basis of the atomic theory and in view of the definition of an atom it is believed that, for example, when the element nitrogen and the element oxygen combine, the actual union involves the combination of atoms of oxygen with atoms of nitrogen. If this is a true picture, then the weight relationships portrayed above must in some way be related to the weights of the atoms concerned. As will be shown later, it is possible to know the actual weight, in grams, of each kind of atom. Such values, however, would be very cumbersome for use in chemical calculations and are so small as to be practically meaningless. If one wished to buy a tract of land and was told that the land under consideration consisted of 6,272,640 sq. in., the prospective buyer would have little knowledge as to the size of the tract. If, on the other hand, he was told that the tract of land consisted of 1 acre (6,272,640 sq. in.), this information would convey a real meaning. By the same token the atom is such an exceedingly small piece of matter that a number representing its true weight in grams would be so small as to carry no real significance to the human mind.

For this and other reasons, it is convenient to assign in an arbitrary manner a value representing the weight of some one kind of atom and thereafter to express the weights of other atoms in relation to this arbitrary standard. The choice of the standard is important since it should be such that

1. The element chosen is one that enters into combination with all (or nearly all) other elements.

2. The numerical value assigned to represent the weight of the atom chosen as a standard will be such that the weights of all other kinds of atoms will be represented by numbers greater than unity and, as nearly as possible, by whole numbers.

The first of these requirements is met if the element oxygen is chosen as the standard, and the second requirement is fulfilled as nearly

as possible by assigning the number 16.0000 to represent the weight of the oxygen atom.

2.4. Relative Combining Weights

Returning, now, to the experimental information that led to the establishment of the law of multiple proportions, it becomes of interest to calculate the weights of nitrogen that are combined with not 1 but rather 16.0000 g. of oxygen in the three oxides of nitrogen.

Oxide	Oxygen, g.	Relative combining weights of nitrogen
Nitrous oxide	16	28.016
Nitric oxide	16	14.008
Nitrogen dioxide	16	7.004

The values representing the weights of nitrogen combined with the arbitrarily chosen standard weight of oxygen are known as *relative combining weights* of nitrogen. Similarly, relative combining weights for chromium may be calculated from the data on compounds of chromium and oxygen.

Oxide	Oxygen, g.	Relative combining weights of chromium
Chromium monoxide	16	52.032
Chromic oxide	16	34.688
Chromium trioxide	16	17.344

Thus, for the elements nitrogen and chromium, there are obtained values for the relative combining weights with a degree of accuracy that is limited only by the accuracy of the methods used in analyzing the compounds under consideration.

The next question that arises has to do with the relation between the relative combining weights and the relative weights of the atoms ("atomic weights") of nitrogen and chromium. It may be stated at this point that the above values for the combining weights will either prove to be equal to the atomic weights or may be made equal to the atomic weights by multiplication by the ratio of two small whole numbers. (This is a natural consequence of the law of multiple proportions.) Before the above question is answered fully, however, some additional experimental information is necessary.

2.5. Approximate Atomic Weights

There are available certain chemical and physical methods by means of which approximate values for the atomic weights may be obtained experimentally. If the element in question is a gas or if the element forms one or more compounds that exist as gases or volatile liquids, a value for the approximate atomic weight of the element may be had without serious experimental difficulty. For example, it may be shown by experiment that the relative weight of the nitrogen *molecule* is approximately 28. If, as pointed out earlier, the molecule of nitrogen consists of 2 atoms (Sec. 1.12), then it follows that the approximate atomic weight of nitrogen is $28 \div 2 = 14$.

Method of DuLong and Petit. For elements which are not gaseous and which do not form volatile compounds, approximate values for the atomic weights may be obtained from a knowledge of the specific heats of the elements. **The specific heat of an element is defined as the quantity of heat** (expressed in calories[1]) **required to raise the temperature of one gram of the element one degree on the centigrade temperature scale.** In 1818, DuLong and Petit discovered that, when the atomic weights of the elements are multiplied by their specific heats, the products are usually numbers between 6 and 7 and that these numbers average about 6.4. Thus,

$$(\text{At. wt.}) \times (\text{specific heat}) = 6.4$$

or

$$\text{At. wt.} = \frac{6.4}{\text{specific heat}}$$

If the atomic weight is unknown and the specific heat of the particular element can be determined experimentally, it is possible to calculate the approximate atomic weight. The specific heat of chromium is found by experiment to be 0.116 calorie. Accordingly, an *approximate* value for the atomic weight of chromium may be calculated.

$$\text{At. wt.} = \frac{6.4}{0.116} = 55$$

With approximate values for the atomic weights of nitrogen and chromium, the relation between the exact relative combining weights and the exact atomic weights may be clarified.

2.6. Exact Relative Atomic Weights

From the study of three nitrogen-oxygen compounds there were obtained three values representing accurate relative combining weights

[1] For definition of the term *calorie*, see Sec. 4.9.

of the element nitrogen, *i.e.*, 28.016, 14.008, and 7.004. Further, it is known that the approximate weight of the nitrogen atom is 14. Consequently, 14.008 must be the exact relative atomic weight of nitrogen, and the other two values for the combining weight of nitrogen should become equal to 14.008 when multiplied by the ratio of two small whole numbers.

$$28.016 \times \frac{1}{2} = 14.008$$

$$7.004 \times \frac{2}{1} = 14.008$$

Up to this point there may have existed a reasonable doubt as to the need for securing three different (but related) values for the combining weight of nitrogen. However, it should now be apparent that, if three such values all lead to the same value for the relative atomic weight of nitrogen (14.008), there should seem little reason to question the correctness of this value. In addition, the result obtained using one value for the combining weight serves as a check on the accuracy of other results.

If the approximate atomic weight of chromium is 55 and the values for the exact relative combining weights of chromium are 52.032, 34.688, and 17.344, then the exact relative atomic weight of chromium must be 52.032, since

$$52.032 \times \frac{1}{1} = 52.032$$

$$34.688 \times \frac{3}{2} = 52.032$$

$$17.344 \times \frac{3}{1} = 52.032$$

2.7. Review

The foregoing discussion is intended to show that the problem of assigning to each kind of atom a numerical value representing the relative weight of that atom involves the following steps:

1. The atom must be recognized as the smallest unit of matter that can participate in a chemical reaction.
2. A suitable standard must be established.
3. From accurate experimental data on the percentage composition of compounds of a given element, accurate values for the relative combining weights are calculated.
4. By some suitable method, an experimental value for the approximate atomic weight of the element must be obtained.

5. With the approximate atomic weight and the exact relative combining weights, the exact relative atomic weight becomes available in the light of the law of multiple proportions.

With this summary in mind, it is suggested that the student re-study Secs. 2.1 to 2.6 before proceeding.

2.8. Meaning of Relative Atomic-weight Values

Since atoms are so small that they may not be seen even with the aid of the most powerful microscope, the chemist cannot work with single atoms. Rather than work with a single atom of nitrogen, it is necessary to work with "bundles" of atoms and of course the chemist chooses bundles of convenient size.

Although the exact values for the relative atomic weights of the elements, being arbitrary, may be expressed in any desired units (grams, pounds, tons, etc.), they are most frequently expressed in grams. Hence, the atomic weight of oxygen, 16,, when expressed in grams, is referred to as the *gram-atomic weight of oxygen* or as *one gram atom of oxygen.* Similarly, 1.008 g. of hydrogen constitutes 1 gram-atomic weight or 1 gram atom of hydrogen. The atomic weight of an element, therefore, is merely the weight of an arbitrarily chosen quantity of that element. A complete list of the most accurate known values for the relative atomic weights of the elements is given on the inside front cover of this book.

Absolute Weights of Atoms. If the bundle of oxygen atoms in terms of which the chemist chooses to work has a weight of 16 g., the question naturally arises as to how many atoms are present in this particular size of bundle. Since atoms are so small, it would certainly be evident that in 16 g. of oxygen, for example, there must be an exceedingly large number of atoms. The actual number is known with a fair degree of accuracy. As determined by a variety of methods which need not be discussed at this point, the number is believed to be 602,000,000,000,000,000,000,000,[1] or expressed more conveniently,

[1] This number, as well as some that follow, illustrates a problem not infrequently encountered in the study of chemistry. It is often necessary to deal with very large or very small numbers, and the task of representing such quantities can become very laborious and cumbersome. To avoid these difficulties, use is made of exponential expressions in which very large or very small numbers are represented in terms of exponents of the number 10. Thus, the number of atoms in a gram-atomic weight of any element is represented as 6.02×10^{23}, which means that the number 6.02 is to be multiplied 23 times by the number 10. If this is done, the result is 602,000,000,000,000,000,000,000. To use another example, the total weight of the atmosphere surrounding the earth has been estimated to be

6.02×10^{23}. This is known as *Avogadro's number.* Because the atomic weights of the other elements are expressed in relation to the atomic weight of oxygen, 1 gram-atomic weight of any element contains 6.02×10^{23} atoms of that element. Thus 1.008 g. of hydrogen must consist of 6.02×10^{23} atoms of hydrogen, and 23 g. (1 gram atom) of sodium must contain 6.02×10^{23} atoms of sodium. This remarkable result enables the chemist to work not only with a known weight of an element but, at the same time, a known number of atoms of that element.

If in 16 g. of oxygen there are 6.02×10^{23} atoms of oxygen, then the absolute weight of the single oxygen atom must be

$$\frac{16}{6.02 \times 10^{23}} = 0.000{,}000{,}000{,}000{,}000{,}000{,}000{,}026 \text{ g. } (2.6 \times 10^{-23} \text{ g.})$$

Similarly, 1 gram-atomic weight of hydrogen (1.008 g.) contains 6.02×10^{23} atoms each having the weight given by

$$\frac{1.008}{6.02 \times 10^{23}} = 0.000{,}000{,}000{,}000{,}000{,}000{,}000{,}001{,}67 \text{ g. } (1.67 \times 10^{-24} \text{ g.})$$

Such numbers should convince even the most skeptical of the wisdom of using the *relative* rather than the *absolute* weights of atoms.

2.9. Relative Weights of Molecules

Since molecules consist of atoms, it follows that the relative weight of a molecule (of an element or a compound) is simply the sum of the relative weights of the atoms in the particular molecule. If, for example, the molecule of the element oxygen contains 2 atoms, each having a relative weight of 16 units, then the weight of the oxygen molecule must be $2 \times 16 = 32$. Similarly, since the water molecule contains 2 atoms of hydrogen and 1 atom of oxygen, the relative weight of the molecule of water must be $(2 \times 1.008) + 16 = 18.016$.

When expressed in grams, the weight of a molecule is referred to as (*a*) 1 gram-molecular weight, (*b*) 1 gram molecule, or (*c*) 1 "mole." Thus, 32 g. of oxygen may be referred to by any of these designations.

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equal to 5,200,000,000,000,000,000,000 g. This number can be represented much more conveniently in exponential form as 5.2×10^{21}.

Small numbers also may be expressed conveniently by the use of negative exponents. Thus, the number 0.000,000,001 may be expressed as 1×10^{-9} since,

$$0.000{,}000{,}001 = \frac{1}{1{,}000{,}000{,}000} = \frac{1}{10^9} = 1 \times 10^{-9}$$

Similarly, the number that represents the absolute weight of the individual oxygen atom is 0.000,000,000,000,000,000,000,026 g. In terms of negative exponents, this number becomes 26×10^{-24} or 2.6×10^{-23}.

Since molecules are formed by the union of atoms, the number of molecules in 1 gram-molecular weight of any substance must be the same as the number of atoms in 1 gram-atomic weight of an element, *i.e.*, 6.02×10^{23}. Hence, in 32 g. of oxygen there are 6.02×10^{23}

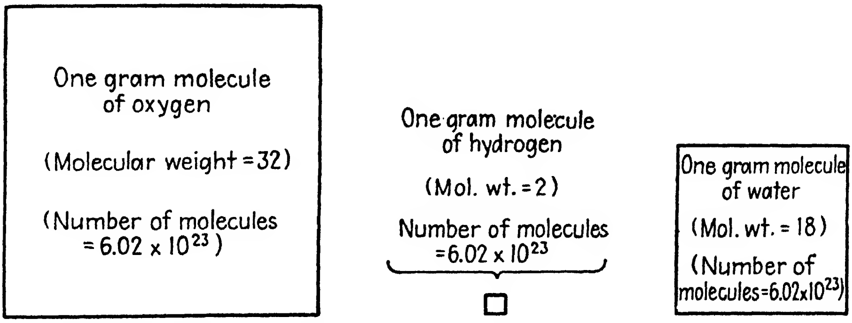


FIG. 7.—Relative weights of molecules. The three squares are drawn to scale in proportion to the relative weights of the oxygen, hydrogen, and water molecules. Note particularly that the number of molecules in 1 gram-molecular weight is the same in all three cases regardless of the marked differences in the gram-molecular weights.

molecules of the element oxygen; in 18.016 g. of water there are 6.02×10^{23} molecules of the compound water (Fig. 7).

EXERCISES

1. List the *experimental* data that are necessary in order to establish a value for the exact relative atomic weight of an element.

2. From the analysis of a compound of sulfur it is found that the exact relative combining weight of sulfur is 8.015. The approximate atomic weight of sulfur is 31. Calculate the exact relative atomic weight of sulfur.

3. Calculations based on a knowledge of the percentage composition of a compound of chlorine and oxygen show that the exact relative combining weight of chlorine in this particular compound is 10.131. If the approximate atomic weight of chlorine is 35, calculate the exact relative atomic weight of chlorine.

4. The approximate weight of the molecule of bromine is 162, and it is known that the molecule of bromine contains 2 atoms. If the exact relative combining weight of bromine is 39.958, calculate the exact relative atomic weight of bromine.

5. The specific heat of copper is 0.09305 cal. Calculate the approximate atomic weight of copper.

6. The analysis of an oxide of copper shows that the oxide consists of 20.11 per cent oxygen and 79.89 per cent copper. Calculate the exact relative combining weight of copper.

7. Using the information from problems 5 and 6, calculate the exact relative atomic weight of copper.

8. Calculate the absolute weight of the copper atom and express the result in both decimal and exponential form.

SUGGESTED READING

Journal of Chemical Education

OESPER, Some Famous Balances, **17,** 312 (1940).

NOYES, Standards of Length, Weight, and Volume in the United States, **5,** 586 (1928).

ROSE, How Small Is a Molecule?, **6,** 1797 (1929).

DAY and SUTTON, The Combining Weight of Copper, **5,** 223 (1928).

BRESCIA and ROSENTHAL, The Atomic Weight of Hydrogen, **16,** 494 (1939).

JOHNSTON, The Avogadro Number, **16,** 333 (1939).

SUNIER, Some Methods of Determining Avogadro's Number, **6,** 299 (1929).

CHAPTER III

SYMBOLS, FORMULAS, EQUATIONS; CHEMICAL CALCULATIONS

The study and the practice of chemistry require frequent reference to a wide variety of chemical substances and chemical changes. The practice of referring to elements and compounds by name and that of providing detailed written descriptions of chemical changes would be exceedingly cumbersome. As a means of providing a more concise

FIG. 8.—Jöns Jakob Berzelius (1779–1848).

system of representation, chemists have developed what may be described as a system of "chemical shorthand." It is essential that the student of chemistry become thoroughly familiar with these methods of representation, since they will be used throughout the beginning course and all subsequent courses in or experience with the subject.

3.1. Symbols

The method now used to represent the atoms of the elements was introduced by the Swedish chemist, Berzelius (Fig. 8), in 1813. The symbols used are derived from the names of the elements by taking the initial letter, the first two letters, or other letters of the English or Latin names. Examples of the use of initial letters of English names are found in the symbols H (hydrogen), O (oxygen), C (carbon), etc. The symbol, K, for the element potassium was taken from the Latin name, *kalium.* The symbol, Ca, is used for the element calcium since the initial letter has already been adopted as the symbol for carbon. Similarly Na (from the Latin *natrium*) is used as the symbol for sodium. The symbol for the element magnesium consists of the first and third letters, Mg. There is given below a list of symbols for the common metals and nonmetals. These symbols will be used repeatedly and should be made a part of the student's vocabulary.

TABLE 3
SYMBOLS FOR COMMON ELEMENTS

Metals		Nonmetals	
Name	Symbol	Name	Symbol
Aluminum	Al	Boron	B
Bismuth	Bi	Bromine	Br
Cadmium	Cd	Carbon	C
Calcium	Ca	Chlorine	Cl
Copper (*cuprum*)	Cu	Fluorine	F
Iron (*ferrum*)	Fe	Hydrogen	H
Lead (*plumbum*)	Pb	Iodine	I
Magnesium	Mg	Nitrogen	N
Manganese	Mn	Oxygen	O
Mercury (*hydrargyrum*)	Hg	Phosphorus	P
Potassium (*kalium*)	K	Silicon	Si
Silver (*argentum*)	Ag	Sulfur	S
Sodium (*natrium*)	Na		
Tin (*stannum*)	Sn		
Zinc	Zn		

Meaning of Symbols. The symbols for the elements are not merely abbreviations. In addition to showing the identity of an element, a symbol represents a definite weight of that element and consequently a definite number of atoms. The symbol H represents 1.008 parts by weight of hydrogen and, therefore, 6.02×10^{23} atoms of hydrogen. Similarly, the symbol K represents 39.1 parts by weight

of potassium (6.02×10^{23} atoms). Since in scientific work weight is usually expressed in grams, the student should acquire the habit of thinking of the symbol for an element as representing 1 gram-atomic weight of that element. For example, each time the symbol O is encountered, it should be interpreted as representing 1 gram atom (16 g.) of the element oxygen.

3.2. Formulas

Just as symbols are used to represent atoms, formulas are used to represent molecules. The molecules so represented may be either elemental or compound. The element oxygen exists, under ordinary conditions, in the form of molecules containing 2 atoms, and this may be shown by writing the symbol for oxygen and appending a subscript written to the right of the symbol, thus, O_2. Similarly, other elemental molecules are represented by formulas H_2, Cl_2, Br_2, etc.

Molecules of compounds are represented by writing side by side the symbols for the atoms that make up the molecules of the compound. Thus, hydrogen chloride is represented by the formula HCl. In the formulas for compounds containing hydrogen or a metal in combination with a nonmetal, the symbol for the nonmetal is usually (but not always) written last in the formula. If the number of one or more kinds of atoms in a given compound is greater than one, this fact must be shown by the formula. Therefore water, which is composed of 2 atoms of hydrogen and 1 atom of oxygen, has the formula H_2O. The formula H_2SO_4 shows that the hydrogen sulfate molecule is composed of 2 atoms of hydrogen, 1 atom of sulfur, and 4 atoms of oxygen. A subscript in a formula refers only to the symbol immediately preceding the subscript, unless placed outside of parentheses. Thus, in the formula for calcium hydroxide, $Ca(OH)_2$, the subscript applies to both the oxygen and the hydrogen.

Meaning of Formulas. Until the student acquires sufficient information to permit a distinction between kinds of chemical union, it is permissible to look upon all formulas as representing molecules. Since formulas are merely collections of symbols that have definite weight significance, it follows that a formula represents not only composition but also a definite weight of the substance concerned. The formula H_2 represents 2.016, (2×1.008) parts by weight of hydrogen, and the formula HCl represents 36.465, ($1.008 + 35.457$) parts by weight of hydrogen chloride. Expressed in grams, these weights are called *gram-molecular weights* (gram molecules, or moles) of hydrogen and hydrogen chloride, respectively. The formula for potassium chlorate, $KClO_3$, shows that the molecule consists of 1 atom of potas-

sium, 1 atom of chlorine, and 3 atoms of oxygen and represents 1 gram-molecular weight, 122.557, [39.1 + 35.457 + (3 × 16)] of potassium chlorate. From this example, it is seen that the (relative) weight of a molecule is simply the sum of the (relative) weights of all the atoms in that molecule.

3.3. Equations

The value of symbols and formulas with their attendant weight significance becomes most apparent in the representation of chemical reactions. Consider the following statement: "Two hundred seven and twenty-one one-hundredths grams of the element lead unite with thirty-two grams of the element sulfur to form two hundred thirty-nine and twenty-one one-hundredths grams of the compound lead sulfide." Expressed in the language of symbols and formulas, this rather cumbersome description of a simple chemical reaction becomes

$$Pb + S = PbS$$

Since the total weight of matter represented to the left of the equality sign (207.21 g. + 32 g.) is equal to the total weight represented to the right (239.21 g.), the above expression may be called an *equation*. To indicate the direction of the chemical change, the equality sign is usually replaced by an arrow which should be interpreted as indicating an equality, thus,

$$Pb + S \rightarrow PbS$$

The foregoing equation is a very simple one and may be written without difficulty. Suppose, however, that it is desired to write an equation representing the formation of water by the union of hydrogen and oxygen. First, there are written the symbols and formulas involved.

$$H + O \rightarrow H_2O \qquad (1)$$

Next, it must be recognized that hydrogen and oxygen exist not as atoms but rather in the form of elemental molecules. Hence the symbols must be replaced by the corresponding formulas.

$$H_2 + O_2 \rightarrow H_2O \qquad (2)$$

Expression (2), however, does not represent a true equality since on the left of the arrow (equality sign) there is shown a total of 2 atoms of oxygen while only 1 atom is shown on the right. Consequently the expression must be adjusted or balanced by the insertion of suitable coefficients,

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (3)$$

leading to a true equality or equation. The overscoring of the symbols or formulas for gases represented in chemical equations is a common practice, but one not followed consistently.

Equation (3) should be read as follows: "Two moles of hydrogen ($2 \times 2.016 = 4.032$ g.) combine with 1 mole of oxygen (32 g.) to form 2 moles ($2 \times 18.016 = 36.032$ g.) of water."

Steps Involved in Writing Equations. From the foregoing example, it appears that the writing of a chemical equation involves the following steps:

1. Write to the left of the arrow the correct symbols or formulas for the substances that undergo change.

2. To the right of the arrow write the correct symbols or formulas for the products of the reaction.

3. Adjust or balance the expression so that a true equality results.

The application of this process may be illustrated by considering the equation representing the decomposition of potassium chlorate. It is necessary first to know (as the result of suitable experiments) that, when potassium chlorate is heated, it decomposes into potassium chloride and oxygen. With this information, the formulas for the substance which undergoes change and the formulas for the products may be written (steps 1 and 2),

$$KClO_3 \rightarrow KCl + \overline{O}_2$$

In order that the total number of atoms of oxygen involved may be such that all of the oxygen may be represented as diatomic molecules, it is necessary to insert the coefficient 2 before the formula for potassium chlorate.

$$2KClO_3 \rightarrow KCl + \overline{O}_2$$

In the balancing of this expression, however, one must recognize the fact that the coefficient inserted modifies all that follows in the formula. Thus, $2KClO_3$ represents a total of 2 atoms of potassium, 2 of chlorine, and 6, (2×3), of oxygen. This same total number of atoms must also be represented on the right of the arrow.

$$2KClO_3 \rightarrow 2KCl + 3\overline{O}_2$$

The resulting expression is a true equation.

Information Provided by Equations. A correctly written chemical equation embodies the following items of information:

1. The identity of each of the substances (commonly known as the *reactants*) that take part in the reaction.

2. The identity of each of the products of the reaction.

3. The weight relationships between the reactants and the products.

Information Not Provided by Equations. Although chemical equations are extremely useful as a convenient means of describing chemical reactions, there are several important items of information that ordinarily cannot be incorporated in equations:

1. An equation gives little or no information concerning the properties of the reactants and products.
2. The fact that a particular chemical equation is written does not mean that the reaction represented will actually occur at all.
3. An equation usually provides no information as to the experimental conditions required for the successful completion of the reaction indicated.
4. An equation provides no indication as to the extent to which a given reaction will proceed in the direction suggested by the arrow.

Although these limitations may at first glance appear to be serious, several means of overcoming certain of these deficiencies will become apparent as the student becomes more familiar with equations and their use.

CHEMICAL CALCULATIONS

In the preceding chapter it was shown that the study of weight relationships led to the establishment of certain fundamentally important laws and to values for the exact relative atomic weights of the elements. This information, together with a knowledge of the nature of symbols, formulas, and equations, leads to the question as to how these relationships may be used in solving problems of a practical character.

3.4. Establishment of Formulas

The formulas for chemical substances are established as the result of experiment. Two kinds of formulas will be considered here: (1) the simplest formula and (2) the true formula. In either case, the initial experimental information required is a knowledge of the percentage composition of the compound in question.

Simplest Formula. Suppose that a quantitative chemical analysis of a compound shows that it consists of 44.89 per cent potassium, 18.37 per cent sulfur, and 36.74 per cent oxygen. In 100 parts by weight of this compound, there are 44.89 parts by weight of potassium, 18.37 parts by weight of sulfur, and 36.74 parts by weight of oxygen. If these relative proportions by weight are divided by the respective atomic weights, the resulting quotients will be the number

of gram atoms of each of the three elements in 100 parts by weight of the compound.

$$\frac{44.89}{39.1} = 1.15 \text{ gram atoms of K}$$

$$\frac{18.37}{32} = 0.57 \text{ gram atom of S}$$

$$\frac{36.74}{16} = 2.29 \text{ gram atoms of O}$$

From this result, it might appear that the formula for the compound is $K_{1.15}S_{0.57}O_{2.29}$. These fractional subscripts may not be used, however, since only whole numbers of atoms unite to form compounds. If the fractional subscripts may not be used as such, they at least express the correct ratio between the three kinds of atoms. The whole-number ratio is obtained by dividing each of the fractional subscripts by the smallest one,

$$\text{K}: \frac{1.15}{0.57} = 2.02$$

$$\text{S}: \frac{0.57}{0.57} = 1.00$$

$$\text{O}: \frac{2.29}{0.57} = 4.02$$

from which it appears that the simplest formula for the compound must be K_2SO_4. The fact that the foregoing quotients do not turn out to be exactly whole numbers is attributed to experimental errors involved in determining the percentage composition of the compound.

True Formula. It happens that the simplest formula, K_2SO_4, derived above, is also the true formula for the compound concerned. Accordingly, another example will be considered to illustrate the derivation of a simplest formula that differs from the true formula.

The analysis of a compound of mercury and chlorine shows that the compound consists of 85.11 per cent mercury and 14.89 per cent chlorine. As in the preceding example, the relative numbers of atoms of mercury and chlorine present are

$$\text{Hg}: \frac{85.11}{200.61} = 0.424; \qquad \frac{0.424}{0.419} = 1.01$$

$$\text{Cl}: \frac{14.89}{35.457} = 0.419; \qquad \frac{0.419}{0.419} = 1.00$$

1 atom of mercury and 1 atom of chlorine. The simplest formula for the compound, therefore, is HgCl.

The question as to whether the simplest formula is the same as the true formula can be answered by a knowledge of the molecular weight of the compound. The weight of the molecule represented by the formula HgCl is $200.61 + 35.457 = 236.067$. An experimental determination of the molecular weight of this compound, however, would show that the molecular weight is approximately 470. Since 470 is nearly twice 236.067, it follows that in each molecule of the compound there must be 2 atoms of mercury and 2 of chlorine. Accordingly, the true formula is Hg_2Cl_2.

3.5. Percentage Composition of Compounds

On many occasions the chemist wishes information concerning the percentage composition of pure chemical compounds. Of course, this information may be supplied by quantitative analysis of the substances concerned but, *if the formula is known*, this same information may be had by a simple calculation. For example, the oxide of iron, Fe_2O_3, has a molecular weight of 159.68 [*i.e.*, the sum of the weights of all the atoms in the molecule: $(2 \times 55.84) + (3 \times 16) = 159.68$]. Hence,

$$\frac{(2 \times 55.84)}{159.68} \times 100\% = 69.94\% \text{ Fe}$$

$$\frac{(3 \times 16)}{159.68} \times 100\% = 30.06\% \text{ O}$$

Suppose that a chemist had available two compounds from which to produce zinc on a commercial scale, ZnS and $ZnCO_3$. All other factors being equal, it would seem desirable to use the compound containing the greater percentage of zinc. This information may be obtained as follows:

$$\begin{aligned} \text{At. wt. of Zn} &= 65.38 \\ \text{Mol. wt. of ZnS} &= 97.38 \\ \text{Mol. wt. of ZnCO}_3 &= 125.38 \end{aligned}$$

$$\text{Zn in ZnS} = \frac{65.38}{97.38} \times 100\% = 67.14\%$$

$$\text{Zn in ZnCO}_3 = \frac{65.38}{125.38} \times 100\% = 52.15\%$$

Other calculations may be made similarly (see exercises at end of chapter).

3.6. Calculations Based on Equations

No single type of chemical calculation is of more far-reaching importance than calculations related to equations. Such calculations

serve many useful purposes. *They serve as a basis for prediction, as a preliminary substitute for experiment, and as a check on the results of experiments.*

If it is desired to produce hydrogen by the reaction between a metal and an acid, certain aspects of the problem may be clarified by a few simple calculations. On the assumption that tin and sulfuric acid are to be the reactants, the following equation may be written to represent the proposed reaction:

Sn	+	H_2SO_4	$\rightarrow$	H_2	+	$SnSO_4$
(at. wt. = 118.7)		(mol. wt. = 98.016)		(mol. wt. = 2.016)		(mol. wt. = 214.7)

Calculation of Weight of Tin Required. Suppose the chemist wishes to produce exactly 25 g. of hydrogen and therefore would like to know how much tin would be necessary to produce this weight of hydrogen. The required information may be had by a simple calculation. The foregoing equation provides the information that 118.7 g. of tin are required to produce 2.016 g. of hydrogen. Now if this is true, then there must be some weight of tin which upon reaction with sulfuric acid will produce 25 g. of hydrogen. Whatever this unknown weight of tin may be, its relationship to 25 g. of hydrogen will be the same as the relation between 118.7 g. of tin and 2.016 g. of hydrogen. If the unknown weight of tin is represented by the traditional x, then these relationships may be expressed as a simple proportion in the following manner:

$$x : 25 :: 118.7 : 2.016$$

or

$$\frac{x}{25} = \frac{118.7}{2.016}$$

Solving for the value of x,

$$\begin{aligned} 2.016x &= 25 \times 118.7 \\ x &= \frac{25 \times 118.7}{2.016} \\ &= 1{,}472 \text{ g. Sn required} \end{aligned}$$

From this result it appears that if 1472 g. of tin are allowed to react with sulfuric acid, there will be produced 25 g. of hydrogen. The correctness of this result may be confirmed readily by experiment.

Calculation of Weight of Hydrogen Sulfate Required. Although it is required that there be present a quantity of hydrogen sulfate (as sulfuric acid) only sufficient (or more than sufficient) to

react completely with the 1472 g. of tin, it might be of interest to know the exact weight of H_2SO_4 consumed in the production of 25 g. of hydrogen. This calculation may be made either on the basis of the weight of tin that reacts or on the basis of the weight of hydrogen formed. With y representing the unknown weight of H_2SO_4, this calculation will be made on both bases:

On basis of Sn that reacts:

$$\frac{y}{1{,}472} = \frac{98.016}{118.7}$$
$$118.7y = 98.016 \times 1{,}472$$
$$y = \frac{98.016 \times 1{,}472}{118.7}$$
$$= 1{,}215 \text{ g. } H_2SO_4 \text{ required}$$

On basis of hydrogen formed:

$$\frac{y}{25} = \frac{98.016}{2.016}$$
$$2.016y = 25 \times 98.016$$
$$y = \frac{25 \times 98.016}{2.016}$$
$$= 1{,}215 \text{ g. } H_2SO_4 \text{ required}$$

Calculation of Weight of Stannous Sulfate Formed. Still another calculation based on this same equation may be made. By a similar calculation, the weight of stannous sulfate ($SnSO_4$) that will be produced as a by-product of the formation of 25 g. of hydrogen may be found. In this case the calculation may be made in relation to (1) the weight of Sn that reacts, (2) the weight of H_2SO_4 that reacts, or (3) the weight of H_2 formed. That is, proportions may be represented in terms of any one of the three factors known. With z representing the weight of $SnSO_4$, any one of the following three proportions may be used to secure the desired result:

(1)

$$\frac{z}{1{,}472} = \frac{214.7}{118.7}$$
$$118.7z = 214.7 \times 1{,}472$$
$$z = \frac{214.7 \times 1{,}472}{118.7}$$
$$= 2{,}662 \text{ g. } SnSO_4 \text{ formed}$$

(2)

$$\frac{z}{1{,}215} = \frac{214.7}{98.016}$$
$$98.016z = 214.7 \times 1{,}215$$
$$z = \frac{214.7 \times 1{,}215}{98.016}$$
$$= 2{,}662 \text{ g. } SnSO_4 \text{ formed}$$

(3)

$$\frac{z}{25} = \frac{214.7}{2.016}$$
$$2.016z = 25 \times 214.7$$
$$z = \frac{25 \times 214.7}{2.016}$$
$$= 2{,}662 \text{ g. } SnSO_4 \text{ formed}$$

Of course, only one of these calculations need be made. The three are presented here only to show the relationship between the quantities of all of the substances involved.

Suggestion. In solving a problem the solution to which depends upon the quantitative relationships exhibited by chemical equations, it is suggested that the following procedure be followed:

1. Write the correct equation representing the chemical reaction involved, and the corresponding weight relationships,

2. Set up a proportion properly related to the equation,

3. Solve the proportion for the quantity required. To illustrate, assume that it is necessary to know the quantity of oxygen that may be produced by the decomposition of 183 g. of potassium chlorate.

(1) $$2KClO_3 \rightarrow 2KCl + 3O_2$$
$$2[39.1 + 35.457 + (3 \times 16)] = 245 \qquad 3(2 \times 16) = 96$$

(2) $$\frac{x}{183} = \frac{96}{245}$$

(3) $$245x = 96 \times 183$$
$$x = \frac{96 \times 183}{245}$$
$$= 71.7 \text{ g. oxygen liberated}$$

Problems of this general type will be encountered frequently, particularly in connection with laboratory work. Again it seems worth while to indicate that, although all the foregoing examples have been concerned with *grams* of various substances, the quantities involved could have been expressed just as readily in terms of other units, such as pounds or tons.

EXERCISES

1. What is the gram-molecular weight of each of the following compounds?

(*a*) MnO_2
(*b*) $Ca(OH)_2$
(*c*) KNO_3
(*d*) $Na_2S_2O_3$
(*e*) $HC_2H_3O_2$
(*f*) $Cu(H_2PO_4)_2$

2. The elements sulfur and oxygen combine to form a compound known as *sulfur trioxide*, the formula of which is SO_3. Write an equation for the reaction.

3. If, in carrying out a chemical reaction, one wished to use exactly 10 moles of cane sugar (formula, $C_{12}H_{22}O_{11}$), what weight (*a*) in grams and (*b*) in pounds would be required?

4. The decomposition of lead dioxide by means of heat leads to the formation of lead monoxide (PbO) and oxygen. Express these facts by means of an equation.

5. When aluminum and sulfuric acid react, the products of the reaction are hydrogen gas and aluminum sulfate, the formula of which is $Al_2(SO_4)_3$. Write an equation for this reaction.

6. A pure compound, upon analysis, is found to contain 43.4 per cent Na, 11.3 per cent C, and 45.3 per cent O. What is the simplest formula for the compound?

7. The analysis of a pure compound shows that it consists of 80.0 per cent carbon and 20.0 per cent hydrogen. (*a*) What is the simplest formula for this compound? (*b*) If the molecular weight of the compound is approximately 30, what is the true formula?

8. Calculate the percentage of S in H_2SO_4.

9. Calculate the percentage of O in $KClO_3$.

10. Calculate the weight of $KClO_3$ required for the production of 10 g. of KCl.

11. By the decomposition of some $KClO_3$ there were obtained 45 g. of oxygen. Calculate the weight of KCl that was also formed in this reaction.

12. The decomposition of mercuric oxide, HgO, by means of heat results in the formation of mercury and oxygen. (*a*) Write the equation for the reaction. (*b*) Calculate the weight of mercury (in tons) that will be produced by the decomposition of 7.56 tons of HgO. (*c*) Express the calculated result in terms of milligrams.

SUGGESTED READING

Journal of Chemical Education

Ewing, What's in a Name?, **15,** 123 (1938).

Hauben, The Derivation of the Names of the Elements, **10,** 227 (1933).

Davis, Count Michael Maier's Use of the Symbolism of Alchemy, **15,** 403 (1938).

Jacobs, On the Writing of Chemical Equations, **15,** 75 (1938).

Simons, Chemical Equations, **3,** 1305 (1926).

Griffin, Calculation of Simplest Formula from Percentage Composition, **10,** 575 (1933).

Brautlecht, Computations in General Chemistry, **4,** 370 (1927).

Spicer, The Solution of Elementary Chemical Problems, **17,** 382 (1940).

Brinkley, Numerical Problems in General Chemistry, **4,** 1283 (1927).

CHAPTER IV

PREPARATION AND PROPERTIES OF OXYGEN; THERMOCHEMISTRY

Of the known chemical elements, oxygen is by far the most abundant and certainly one of the most important. Elemental oxygen is present in air to the extent of approximately 21 per cent and makes up more than 50 per cent of the earth's crust. This element also constitutes a significant part of such familiar materials as wood, ores, cotton, and foodstuffs. Oxygen and compounds of oxygen are essential in such important processes as animal and plant respiration, the burning of fuels, the corrosion or rusting of metals and alloys, and the decay of animal and vegetable matter. Historically, the English clergyman, Priestley (Fig. 9), is commonly credited with the discovery of oxygen. There is ample evidence, however, to indicate that this element was first prepared and recognized as an elemental substance by the Swedish chemist, Scheele (Fig. 10).

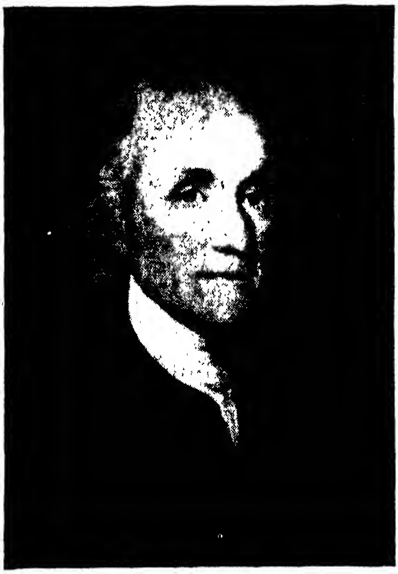


FIG. 9.—Joseph Priestley (1733–1804). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

4.1. Preparation of Oxygen

Methods for the production of elemental or compound substances may be classified as (*a*) laboratory methods and (*b*) commercial methods. The choice of procedure employed in any given instance is governed by numerous factors such as the quantity and the purity of the material required, cost, and convenience. For small-scale use in the laboratory, methods which result in pure products and which are convenient to use are usually preferred regardless of the cost involved.

Separation of Oxygen from Air. Dry air is a mixture consisting of roughly 21 per cent oxygen and 78 per cent nitrogen by volume. The remaining 1 per cent consists of carbon dioxide (CO_2) and a group of elements which are usually referred to as "the inert gases of the atmosphere," *viz.*, helium (He), neon (Ne), argon (A), krypton (Kr), and xenon (Xe).

Under suitable experimental conditions, air may be caused to liquefy. When the resulting liquid mixture is allowed to boil, the various components pass from the liquid to the gaseous state at different temperatures. After a quantity of "liquid air" has been allowed to boil until a little more than four-fifths has vaporized, the liquid that remains is oxygen of sufficient purity for most industrial uses. The greater part of the oxygen sold commercially is secured from the air.

FIG. 10.—Karl Wilhelm Scheele (1742–1786).

Preparation of Oxygen by the Decomposition of Water. Water is a cheap, abundant "raw material" which is exceptionally rich in oxygen (nearly 90 per cent by weight). By subjecting water to the action of an electric current, water may be decomposed as shown by the equation,

$$2H_2O \rightarrow 2H_2 + O_2$$

This method for the production of oxygen is adaptable to both laboratory and commercial-scale use.

Preparation of Oxygen by the Decomposition of Other Compounds of Oxygen. The most convenient method for the production of pure oxygen on a laboratory scale involves the thermal decomposition of certain compounds that contain oxygen. It has already been shown that oxygen is liberated when potassium chlorate is decomposed by heat. In a similar manner, other compounds containing oxygen may be decomposed. It should not be inferred, however, that all compounds of oxygen are decomposed with the liberation of elemental oxygen. Many such compounds will, when heated, give up only a part of their oxygen while still others yield products other than the element oxygen.

There are given below five equations representing reactions that yield oxygen gas. All these reactions require that the solid reactants be heated to elevated temperatures which differ depending upon the particular compound used as the source of oxygen.

$2HgO$ Mercuric oxide	$\rightarrow$	$2Hg$	$+ \overline{O}_2$
$2PbO_2$ Lead dioxide	$\rightarrow$	$2PbO$ Lead monoxide	$+ \overline{O}_2$
$3MnO_2$ Manganese dioxide	$\rightarrow$	Mn_3O_4 Manganous-manganic oxide	$+ \overline{O}_2$
$2KNO_3$ Potassium nitrate	$\rightarrow$	$2KNO_2$ Potassium nitrite	$+ \overline{O}_2$

(It is not necessary that the student memorize these or other equations. When the names and formulas of the reactants and products have been learned, the equations may be written by application of the method previously outlined.)

4.2. Catalysis

When white solid crystals of pure potassium chlorate are heated, the solid melts when the temperature reaches 200°C. At this temperature, however, oxygen is not liberated at any appreciable rate. In order for the decomposition to occur rapidly it is necessary to raise the temperature above 360°. If to pure potassium chlorate there is added a very small quantity of manganese dioxide, it will be found that the $KClO_3$ is decomposed rapidly at about 200°. That is, in the presence of a foreign substance, manganese dioxide, the rapid decomposition of potassium chlorate occurs at a considerably lower temperature than that required in the absence of the foreign substance. Consider the two parallel situations:

$$\text{At } 200°\text{C.}\begin{cases}\text{KClO}_3 \text{ alone decomposes } \textit{very slowly}\\ \text{KClO}_3 \text{ in the presence of MnO}_2 \text{ decomposes } \textit{very rapidly}\end{cases}$$

Before this striking result can be explained, it is necessary also to know that upon completion of the decomposition of the $KClO_3$, the MnO_2

can be recovered unchanged. As far as can be ascertained, the MnO_2 is the same material in every respect as that originally mixed with the potassium chlorate and has not been altered in any way. The MnO_2, however, by virtue of its presence is seen to be capable of speeding up the decomposition of potassium chlorate. This is an example of catalytic action or *catalysis.* A similar result would have been obtained by using ferric oxide (Fe_2O_3) or potassium dichromate ($K_2Cr_2O_7$) in place of the manganese dioxide. The use of manganese dioxide as a catalyst for the preparation of oxygen by the decomposition of potassium chlorate may appear to be subject to criticism on the grounds that MnO_2 will itself yield oxygen when heated. Such criticism is rendered invalid by the fact that the decomposition temperature of manganese dioxide is much higher (535°C.) than the temperature employed in the catalyzed decomposition of $KClO_3$ and by the fact that, after use as a catalyst, the MnO_2 can be recovered unchanged.

In addition to substances that accelerate certain chemical reactions there are some that decrease the rates of certain reactions. The presence of a foreign substance that is not itself consumed in the reaction may result in (1) an increase, (2) a decrease, or (3) no change, in the rate of a given reaction. Accordingly, **a catalyst may be defined as a substance which alters the rate of a chemical reaction and which is not consumed in the reaction.** It is becoming increasingly common to restrict the term *catalyst* to those substances which increase the rates of reactions and to describe those which decrease reaction rates as *retarders* or *inhibitors.*

In general, catalysts and retarders are very specific in their behavior. A substance that catalyzes one reaction may be wholly without effect in another reaction. Similarly, a material that is a catalyst for one particular reaction may act as an inhibitor for another. The entire subject of catalysis is one of the most intriguing and least understood phases of the science of chemistry.

Applications of Catalysis. In connection with commercial chemical processes, applications of both catalysts and inhibitors are numerous. In fact, many important industrial products are available at low cost only because of catalytic action. Finely divided platinum, ferric oxide, vanadium pentoxide (V_2O_5), and oxides of nitrogen are used to accelerate the combination of sulfur dioxide and oxygen in the manufacture of sulfuric acid. One method for the commercial production of ammonia (NH_3) depends upon the fact that the union of nitrogen and hydrogen is catalyzed by metals such as platinum or uranium. Liquid vegetable oils such as cottonseed oil are changed

into semisolid substitutes (such as Crisco, Snowdrift, or Spry) for animal fats by reaction with hydrogen in the presence of a catalyst consisting of finely divided nickel.

There are also many examples of the use of inhibitors. Many food and drug products deteriorate when exposed to the air unless suitable inhibitors or retarders, such as sodium benzoate, are added. The useful life of articles made of rubber is increased by the presence of retarders which decrease the rate at which the rubber is attacked by atmospheric oxygen.

4.3. Properties of Oxygen

Under ordinary conditions of temperature and pressure, oxygen is a colorless, odorless gas which is slightly heavier than air and which dissolves in water to the extent of only 3 volumes of oxygen per 100 volumes of water. When cooled to $-182.963°C.$, oxygen passes from the gaseous to the liquid state. Liquid oxygen has a steel-blue color and is highly magnetic. At $-218.4°C.$, liquid oxygen solidifies. Other properties which may be listed here and the significance of which will be explained later are boiling temperature = $-182.963°C.$; melting temperature = $-218.4°C.$; critical temperature = $-118.8°C.$; density = 0.0014292 g. per cc. All the properties mentioned thus far are of the type known as *physical properties.* There are also those properties which are known as *chemical properties.* The chief chemical property of oxygen is its tendency to combine with other elements to form compounds known as *oxides.* It has already been pointed out that under ordinary conditions oxygen gas consists of molecules containing 2 atoms each.

4.4. Uses of Oxygen

The annual production of oxygen in the United States amounts to approximately 2,500 million cubic feet, most of which is obtained from liquid air. The bulk of this oxygen is used in the production of high temperatures in the burning of gaseous fuels such as acetylene in the oxyacetylene torch which is used in the cutting and welding of metals and alloys. Minor uses center about the problem of supplying adequate oxygen for human respiration under conditions where the quantity of oxygen in the atmosphere is insufficient. Thus, portable tanks of oxygen are carried by aviators for use at very high altitudes, by mine rescue squads following explosions, by the crews of submarines that must remain submerged over considerable periods of time, and by divers engaged in undersea work. The physician frequently adminis-

ters oxygen in the treatment of respiratory ailments, such as pneumonia.

4.5. Ozone

When pure dry oxygen or dry air is passed between two electrically charged plates arranged as shown in Fig. 11, a portion of the oxygen is converted to a substance known as *ozone,* which has the formula, O_3.

$$3O_2 + \text{energy} \rightarrow 2O_3$$

During storms, small traces of ozone are produced in the atmosphere by lightning discharges. At ordinary temperatures, ozone is a pale-blue gas having a characteristic "fresh" odor. It is about 1.5 times as heavy as ordinary oxygen and is much more active chemically, as is

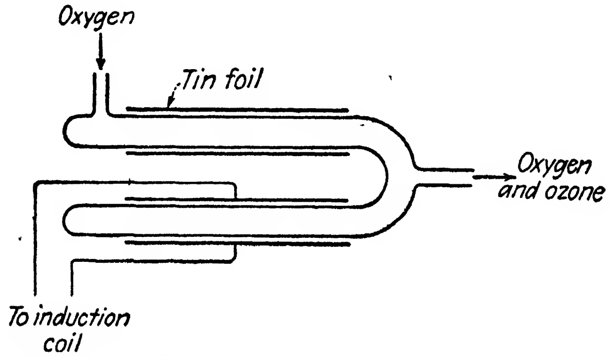


FIG. 11.—Apparatus for the preparation of ozone by the method of Siemens.

shown by the fact that it will combine readily with metals such as silver and mercury which unite with ordinary oxygen only very slowly. Ozone is very unstable and decomposes into ordinary oxygen,

$$2O_3 \rightarrow 3O_2$$

a reaction which proceeds rapidly at elevated temperatures and which is catalyzed by water vapor. Pure ozone decomposes with explosive violence. Because of the difficulty and high cost of producing ozone, the pure substance is not used commercially; however, air containing appreciable quantities of ozone ("ozonized air") is used in certain European countries for the sterilization of drinking water. Ozonized air has also been used to a limited extent as a bleaching agent, as a deodorizer, and as a disinfectant.

The existence of an elemental substance in two or more forms having distinctly different properties is not uncommon. These different forms are called *allotropic modifications* of the element. The element

oxygen is one that exhibits *allotropy* since the two allotropic modifications, O_2 and O_3, are known. Several of the nonmetals and metals exhibit allotropy and certain of these cases will be studied later in some detail.

4.6. Combustion

All the elements excepting the inert gases combine with oxygen to form oxides. These oxides are classified as *binary* compounds since they contain only two kinds of elements. Thus, **an oxide may be defined as a binary compound which contains the element oxygen.** This process of combination with oxygen is known as *oxidation*,[1] and the substance that unites with oxygen is said to be *oxidized*. The union of elements (or of compounds) with oxygen is accompanied by either the absorption or the liberation of energy in the form of heat. The oxidation of a given quantity of matter involves the same quantity of heat (liberated or absorbed) regardless of the rate at which the oxidation occurs. **Rapid oxidation accompanied by the liberation of energy in the form of heat and light is called combustion.**

When heat is liberated in an oxidation reaction, the atmosphere and surrounding objects absorb the liberated heat with the result that the temperature of the material undergoing oxidation does not become very high. If, however, the substance being oxidized is so insulated that the heat evolved cannot escape readily, the temperature may increase to such an extent that the substances burst into flame, *i.e.*, *spontaneous combustion* occurs. Oil-soaked rags frequently are involved in spontaneous combustion because the oil oxidizes slowly and the rags provide insulation which prevents the escape of the heat liberated. As the heat accumulates, the temperature is increased and the oxidation proceeds progressively more rapidly until finally the ignition temperature of the mass is reached and it bursts into flame.

4.7. Production and Uses of the Inert Gases of the Atmosphere

Although the inert gases are present in the atmosphere only to the extent of about 1 per cent (by volume), methods have been devised whereby helium, neon, argon, krypton, and xenon may be obtained in a fair degree of purity. These gaseous elements, which were discovered by the English chemist, Ramsay, and his co-workers, are unique among the chemical elements in that these inert gases exhibit

[1] The term *oxidation* is not, however, restricted to reactions involving oxygen. Broader implications of the term will be considered later and will be shown to embrace a broad class of important chemical reactions.

little or no tendency toward entering into chemical combination. Since these elements are inactive chemically, they must be separated and purified by physical rather than by chemical methods.

Helium is obtained from natural gas in plants owned and operated by the government and located in Kansas and Texas (Fig. 12). The gases from certain wells in this region contain considerable quantities of nitrogen and approximately 1 per cent helium. The latter is separated by liquefying all the other gases, and the gaseous helium (which boils at the very low temperature of −268.90°C.) is then separated from the other liquefied gases. In this manner about 30 million cubic feet of helium are produced annually at a cost of only about 5 cents per

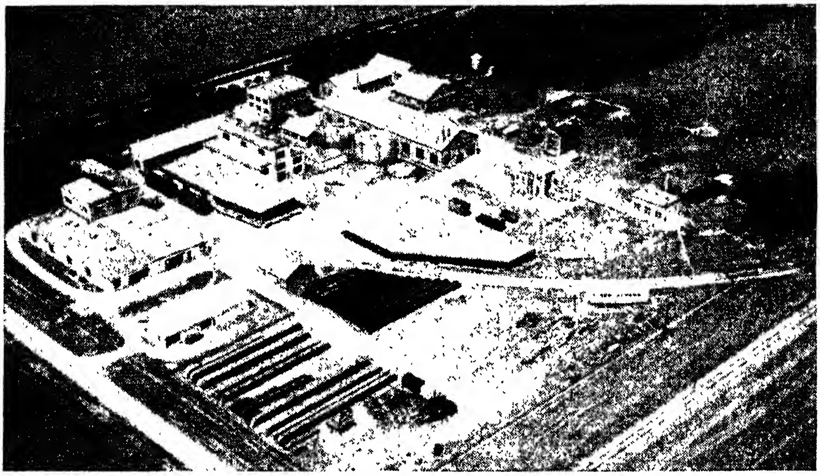


FIG. 12.—Aerial view of a helium plant located at Amarillo, Tex. (*Courtesy of U. S. Department of the Interior, Bureau of Mines.*)

cubic foot, whereas, in 1918, the use of less efficient methods involved a production cost of approximately $2500 per cubic foot. Helium is used chiefly in the inflation of observation ballons and other lighter-than-air craft. Its advantage over hydrogen for this purpose lies in the fact that helium will not burn. Although twice as heavy as hydrogen, helium has 92.6 per cent of the "lifting power" of hydrogen.

Neon, argon, krypton, and xenon are produced commercially by the fractional distillation or fractional liquefaction of air. Neon (and to some extent helium and argon) is used in the so-called *neon signs* so widely used in advertising, in airplane beacons, etc. Such signs may be operated at low cost and penetrate fog much better than ordinary electric lights. The different colors produced depend upon the colors of the glass tubes used, the relative quantities of neon, argon, and helium employed, and the presence of mercury vapor and other

foreign substances. Argon is used chiefly in filling electric light bulbs. Nitrogen was formerly used for this purpose, but the bulbs filled with argon are much more efficient, serve longer, and produce a light more like natural daylight. There are at present no important uses for krypton and xenon because of their scarcity and high cost of production. There is, however, evidence that electric light bulbs filled with these two gases are even more efficient than those filled with argon.

THERMOCHEMISTRY

4.8. Forms of Energy

It has already been pointed out that every chemical reaction is accompanied by a characteristic energy change. Energy is usually defined as the ability of a body to perform work and is recognized in many different forms such as electrical energy, mechanical energy, chemical energy, kinetic energy, or potential energy. Kinetic energy is energy possessed by a body in motion and is equal to one-half the product of its mass by the square of its velocity,

$$\text{Kinetic energy (K.E.)} = \tfrac{1}{2}mv^2$$

Potential energy is energy that is possessed by a body by virtue of its position. Chemical energy is merely a special name for the kinetic and potential energies which are possessed by atoms and molecules and which become evident when these atoms and molecules undergo chemical change.

The law of conservation of energy holds that energy may be neither created nor destroyed. One form of energy may be converted into one or more other forms, but the total quantity of energy is thereby unchanged. Thus, the kinetic energy of a waterfall may be converted into electrical energy, heat energy may be converted to mechanical energy, etc.

4.9. Exothermal and Endothermal Reactions

The energy changes that accompany chemical reactions are usually expressed in terms of heat energy. Heat energy is measured in terms of a unit known as the *calorie*, which is the quantity of heat required to raise the temperature of 1 g. of water from 15° to 16°C. It is frequently desired to incorporate in chemical equations information as to the number of calories of heat liberated or absorbed, and equations so written are usually called *thermochemical equations.* There is no sound basis for predicting whether heat will be liberated or absorbed in any given chemical reaction; this information must be obtained by experiment.

Chemical changes in which heat is given up to the surroundings (liberated) are known as *exothermal* reactions. Since heat is liberated, the heat may be considered as a product of the reaction and so represented in the thermochemical equation, thus,

$$C + \overline{O}_2 \rightarrow \overline{CO}_2 + 94{,}237 \text{ cal.}$$

This equation provides the information that the union of 12 g. of carbon (in the form of graphite) and 32 g. of oxygen results in the formation of 44 g. of carbon dioxide and the liberation of 94,237 cal. of heat. This quantity of heat is liberated regardless of whether the 12 g. of carbon are burned slowly or rapidly. Other examples of exothermal reactions are given by the equations,

$$\begin{array}{llll}
2\overline{H}_2 & + \overline{O}_2 & \rightarrow 2H_2O & + 136{,}720 \text{ cal.} \\
S & + \overline{O}_2 & \rightarrow \overline{SO}_2 & + 70{,}940 \text{ cal.} \\
4P & + 5\overline{O}_2 & \rightarrow 2P_2O_5 & + 739{,}800 \text{ cal.} \\
4Na & + \overline{O}_2 & \rightarrow 2Na_2O & + 200{,}520 \text{ cal.} \\
2KClO_3 & \rightarrow 2KCl & + 3\overline{O}_2 & + 26{,}260 \text{ cal.} \\
2PbO_2 & \rightarrow 2PbO & + \overline{O}_2 & + 75{,}400 \text{ cal.}
\end{array}$$

From experience in the laboratory the student may have learned that the decomposition of $KClO_3$ requires the application of heat and may wonder why this should be so in the case of an exothermal reaction. As pointed out in Sec. 4.2, the heat applied serves merely to raise the temperature to an extent such that the *rate* of the decomposition becomes appreciable. Thereafter, the reaction does proceed with liberation of heat.

If, on the other hand, heat is absorbed from the surroundings during a chemical change, the reaction is said to be an *endothermal* reaction. Since the heat energy in such a case is required for the occurrence of the reaction, the heat may be looked upon as one of the reactants and accordingly represented on the left of the arrow in the thermochemical equation,

$$2HgO + 43{,}200 \text{ cal.} \rightarrow 2Hg + \overline{O}_2$$
$$2KNO_3 + 61{,}120 \text{ cal.} \rightarrow 2KNO_2 + \overline{O}_2$$

These equations show that definite quantities of heat are absorbed in the decomposition of definite quantities of mercuric oxide and potassium nitrate. For no apparent good reason other than the fact that it has become conventional practice to do so, heat absorbed in endothermal reactions is most commonly represented to the right of the arrow in the thermochemical equation. Thus, the foregoing equations may be written in conventional form by transposition of the

heat term to the right-hand side of the arrow (equality sign) with the necessary change in sign.

$$2HgO \rightarrow 2Hg + O_2 - 43{,}200 \text{ cal.}$$
$$2KNO_3 \rightarrow 2KNO_2 + O_2 - 61{,}120 \text{ cal.}$$

Hence, the *sign* of the heat term indicates whether the reaction is exothermal or endothermal.

Information concerning the quantity of heat energy involved in chemical reactions is important because **the tendency toward the occurrence of a chemical change is roughly proportional to the quantity of heat liberated.** Thus, if a large quantity of heat is liberated in a given reaction, the tendency for this reaction to occur is relatively great; if the quantity of heat liberated is small, the tendency for such a reaction to occur is correspondingly small.

4.10. Distinction between Heat and Temperature

Heat has been defined as a form of energy which may be measured in terms of calories. Hence, the use of the term *heat* carries the implication of *quantity*. Care should be exercised in order that the terms *heat* and *temperature* may not be confused. Suppose that two containers are filled with water and heated (supplied with calories) at the same rate until the water in the smaller container boils. If the same number of calories is supplied to the contents of both containers, the *temperature* of the boiling water in the smaller container will be 100°C. while that of the water in the larger container will be somewhat less than 100°. Although the same number of calories is transferred to both bodies of water, the heat supplied to the larger body of water is not sufficient to cause boiling because this heat is distributed throughout a larger volume of water. Thus, temperature is a measure of the extent to which calories are piled up on or within a body of matter or the extent to which these heat units are concentrated within a given volume. Heat, then, is a quantity factor, while temperature is an *intensity factor*.

4.11. Measurement of Temperature

Temperature is commonly (but not always) measured by an instrument called a *thermometer*, usually consisting of a glass bulb which is attached to a long glass tube having a small capillary bore and which is graduated in divisions called *degrees*. The glass bulb is filled with mercury or other liquid that will expand when heated and rise in the small opening in the glass tube. The Fahrenheit temperature scale is used in the home and to a great extent in industrial plants

in English-speaking countries. This scale is constructed in a wholly arbitrary manner by marking the position of the thread of mercury in the thermometer stem when the bulb is in contact with melting ice and calling this temperature 32°. Similarly, the temperature of boiling water on this scale is called 212°, and the intervening distance on the thermometer stem (as well as above 212° and below 32°) is divided into scale divisions of equal length.

The centigrade scale has been arbitrarily established in the same manner except that the temperature of melting ice is taken as 0° and the temperature of boiling water is called 100°. This scale is the one most commonly used in scientific work throughout the world. It is frequently necessary to convert temperature readings from one thermometer scale to another. A comparison of the Fahrenheit and centigrade scales (Fig. 13) provides a basis for such a conversion.

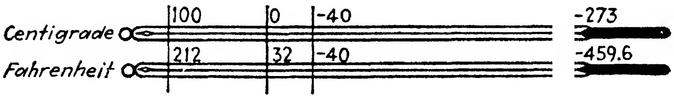


FIG. 13.—Comparison of centigrade and Fahrenheit temperature scales.

Since each division on the Fahrenheit scale is five-ninths of one division on the centigrade scale, Fahrenheit temperatures may be converted to centigrade by the following relationship:

$$°C. = \tfrac{5}{9}\,(°F - 32)$$

or

$$°F. = \tfrac{9}{5}(°C.) + 32$$

It should be understood clearly that both of these are arbitrary man-made temperature scales. Another scale which has its foundation in the natural behavior of matter will be considered in the next chapter.

4.12. Temperature and Chemical Change

The occurrence of chemical reactions is believed to be dependent upon the ability of molecules to move through space as a result of their kinetic energy. If the temperature of a substance is increased (*i.e.*, if heat energy is supplied), the heat energy is converted to, and hence serves to increase, the kinetic energy of the molecules. Since the mass of the individual molecules does not change (K.E. = $\frac{1}{2}mv^2$), the velocity of their motion must be increased. Accordingly, an increase in temperature increases the kinetic energy of the molecules with a corresponding increase in the rate at which the molecules can undergo change.

Although not a hard and fast rule, the following is a very useful

generalization with respect to the influence of temperature upon the rates of chemical reactions in general: for reactions occurring at ordinary temperatures, the rate of reaction is approximately doubled by a temperature increase of 10°C.

4.13. Other Factors that Influence the Rates of Chemical Reactions

In addition to temperature, two factors that influence the rates of chemical changes are (1) concentration and (2) catalysis. The influence of catalysts has already been discussed.

By the term *concentration* is meant the quantity of matter contained in some definite volume. Concentration might be expressed in terms

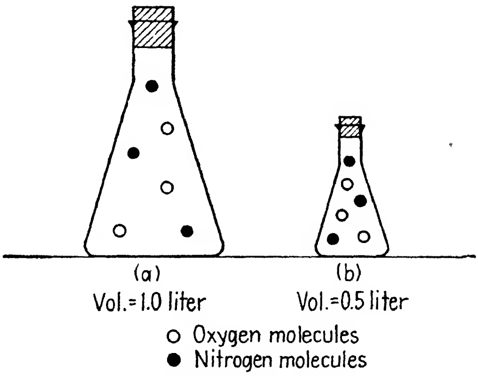


FIG. 14.—Concentration of gas molecules.

of the number of grams of a substance contained in a volume of 1 cc. or 1 liter. It might be useful also to express concentration in terms of the number of molecules or atoms of a substance contained in some unit of volume such as a cubic centimeter or a liter.

The manner in which the rate of a chemical reaction may be influenced by a change in concentration may be understood by considering one or two simple examples. If a wooden splint is heated in air (which contains about 21 per cent of oxygen) until the splint glows and then is thrust into a test tube containing pure oxygen, the glowing splint will burst into flame. The reason for this is that the glowing splint has been brought into an atmosphere that is richer in oxygen than is ordinary air, *i.e.*, the concentration of oxygen is greater in the test tube and accordingly the union of the wood with oxygen proceeds at a greater rate. To consider another example, suppose that it is desired to produce nitric oxide by the direct union of nitrogen and oxygen.

$$\bar{N}_2 + \bar{O}_2 \rightarrow 2\overline{NO}$$

If 3 molecules of nitrogen and 3 molecules of oxygen are mixed in a closed 1-liter flask (Fig. 14), the reaction will proceed at a definite rate which depends upon the temperature and upon the frequency with which the molecules meet as they move through space. If, now, the same number of molecules of nitrogen and oxygen are placed in a ½-liter flask at the same temperature, the reaction will proceed more rapidly than in the first case because the concentration of the reacting substances has been increased. In the ½-liter flask, the concentration (number of molecules per unit of volume) is twice as great as in the 1-liter flask, and the molecules of nitrogen and oxygen will meet more frequently and therefore will react more rapidly.

The rates of reaction of solid substances are also dependent upon their state of subdivision. A large compact lump of a solid material cannot, for example, react with oxygen so rapidly as would be the case if the large lump were first ground to a fine powder. A lump of coal is burned only slowly, but finely powdered coal may be caused to react with ordinary air at an explosive rate—a chemical change that is involved in many mine explosions. The more finely subdivided materials react at a greater rate because so much more surface is exposed.

EXERCISES

1. Define the following terms: (*a*) catalyst, (*b*) accelerator, (*c*) retarder, (*d*) combustion, (*e*) kinetic energy, (*f*) potential energy, (*g*) chemical energy, (*h*) concentration.

2. What are allotropic modifications of an element?

3. Distinguish between (*a*) positive and negative catalysis, (*b*) exothermal and endothermal reactions, (*c*) heat and temperature.

4. List three experimental conditions that influence the rates of chemical reactions.

5. Give important commercial uses for (*a*) oxygen, (*b*) helium, (*c*) neon, (*d*) argon.

6. Convert the following centigrade temperatures to the corresponding Fahrenheit temperatures: (*a*) 86°C., (*b*) 438°C., (*c*) −73°C.

7. Convert the following Fahrenheit temperatures to the corresponding centigrade temperatures: (*a*) 100°F., (*b*) −162°F., (*c*) 0°F.

8. Calculate the percentage of oxygen in (*a*) potassium chlorate, (*b*) manganese dioxide, (*c*) potassium nitrate.

9. Calculate the weight of oxygen which may be obtained by heating 100 lb. of each of the above compounds.

10. If potassium chlorate costs 45 cents per pound, manganese dioxide costs 24 cents per pound, and potassium nitrate costs 34 cents per pound, which of these three substances is the cheapest source of oxygen if the cost of the oxygen compound is the only factor involved?

11. What other factors might need to be considered in deciding which of these three compounds would be the cheapest to use in the production of oxygen on a large scale?

12. At what temperature is the value on the centigrade scale identical with that on the Fahrenheit scale?

SUGGESTED READING

Journal of Chemical Education

MEYER, Chromium Trioxide as a Catalyst in Potassium Chlorate Decomposition, **17**, 494 (1940).

CURRIER, Some Catalytic Reactions, **17**, 262 (1940).

MITCHELL, Heterogeneous Catalysis, **9**, 261 (1932).

ALEXANDER, Some Aspects of Catalysis, **9**, 2026 (1932).

LIVINGSTON, An Introduction to Chemical Catalysis in Heterogeneous Systems, **7**, 2887 (1930).

HENDRICK, Catalysis—A New Factor in Industry, **2**, 631 (1925).

CARTER and REINHARD, Modern Uses of Oxygen, **19**, 91 (1942).

WORSTELL, On Ozone, **9**, 291 (1932).

GROSS, Rare Gases in Everyday Use, **18**, 533 (1941).

SEIBEL, Helium and Natural Gas, **3**, 45 (1926).

BARTLETT, Accomplishing Much by Doing Nothing, **4**, 1376 (1927).

BROWN, Some Early Thermometers, **11**, 448 (1934).

BARNETT, A Brief History of Thermometry, **18**, 358 (1941).

CLINTON, The Energy Factor in Chemical Changes, **8**, 683 (1931).

Industrial and Engineering Chemistry

CADY, Beginnings of the Helium Industry, **30**, 845 (1938).

SEIBEL, Production of Helium at Amarillo, **30**, 848 (1938).

METZGER, Traces from Tons, **27**, 112 (1935).

CHAPTER V

PROPERTIES OF GASES

Each of the three states of matter has certain characteristic properties which are different from those of the other two. Solids are relatively dense materials and retain their form regardless of the size or shape of the container in which they are placed (Fig. 15). Liquids have the ability to flow and to assume the shape of any vessel in all except the vertical direction. Gases differ from liquids and solids in that they enjoy relatively unrestricted motion and are capable of moving through space at high velocities and of distributing themselves uniformly in all directions throughout the vessel in which they are confined.

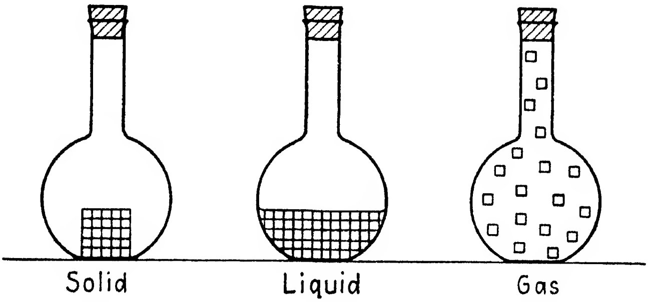


FIG. 15.—Comparison of solid, liquid, and gas.

Although man lives in a gaseous atmosphere, he is less aware of the existence of gases than of the existence of liquids and solids. This is largely due to the fact that many of the most common gases are colorless, odorless, and of low density.

5.1. Regularities Observed in the Behavior of Gases

Progress in the understanding of chemical changes requires a knowledge of the make-up or structure of the various forms of matter. It has been known for a long time that the structure of gaseous substances is much simpler and more easily studied in the laboratory than the structure of either liquids or solids. Furthermore, much of the information gained from the study of gases is of value in attempts to learn of the structure of liquids and solids. Experiments performed

by scientists over a long period of time have shown that all the common gases behave very much (although not exactly) alike. For example, it is a familiar fact that confined gases exert pressure on the walls of their containers. All gases tend to expand when heated. These and other facts suggest that the structures of different gases must be very similar.

5.2. Kinetic-molecular Theory

In an effort to explain the behavior of matter in the gaseous condition, there has been developed a mental picture known as the *kinetic-molecular theory.* To understand this theory and to utilize it in the study of gases require the exercise of one's imagination. The principal ideas that make up the kinetic-molecular theory may be outlined as follows:

1. *A gas is believed to consist of molecules separated by relatively wide empty spaces.*

2. *The diameters of the gas molecules are very small in comparison with the distance between molecules.* These ideas are wholly reasonable in view of the low density of gases. If this were not the case, one could not walk through a gaseous atmosphere without encountering resistance similar to that met in walking through water.

3. *Gas molecules are in a constant state of rapid and chaotic motion.*

4. *Gas molecules move in straight lines until they collide with other molecules or with the walls of the containing vessel.* The sum of the impacts of billions of moving gas molecules against the walls of a closed container constitutes the *pressure* exerted by a confined gas. The walls of a vessel filled with a gas may be thought of as being constantly "bombarded" by rapidly moving molecules.

5. *When gas molecules collide, they rebound without loss of energy.* If this were not true, gas molecules would suffer a loss in kinetic energy upon collision and finally would be incapable of existing in the gaseous state. It is largely because of the "elastic" character of these collisions that gas molecules do not settle to the bottoms of their containers under the influence of gravity.

6. *The average kinetic energy of all different kinds of gas molecules is the same.* Since different kinds of gas molecules have different masses, their velocities must be such as to give all the same *average* kinetic energy (K.E. = $\frac{1}{2}mv^2$) at any specified temperature. This means simply that light molecules must have velocities of motion greater than those of heavy molecules.

7. *There exists between gas molecules a force of attraction which, at ordinary temperatures and pressures, is small in comparison with the*

kinetic energy. This force of attraction or cohesion is ordinarily so small that it is incapable of overcoming the influence of the kinetic energy which serves to keep the molecules apart and in motion.

At first glance, this theory may appear to be somewhat visionary, particularly in view of the fact that it is impossible to observe the behavior of any single molecule or any small number of molecules. Nevertheless, the more that is learned about the behavior of gases, the more sound does this theory appear to be. The ultimate test of any theory is the success attendant upon its use in the interpretation of the results of actual experiments.

5.3. Gas Laws

The study of gases has led to the formulation of a number of *laws* which serve to describe the behavior of substances in the gaseous condition. These laws may be stated either in words or in the form of exact mathematical expressions. It should be understood clearly that these are not man-made laws. They are simply concise descriptions of observed habits of nature; they *describe* but do not *govern.*

5.4. Measurement of Pressure

A familiar example of the exertion of pressure by gases is the pressure of the atmosphere. It is well known that the pressure exerted by the gaseous atmosphere is less at the top of a mountain than at the bottom. The pressure exerted by the atmosphere (or any other gas) may be measured by an instrument known as the *barometer*, a simple form of which is shown in Fig. 16. A glass tube 800 mm. (about 31.5 in.) in length is closed at one end, filled with mercury, inverted, and the open end placed beneath the surface of mercury contained in an open vessel. The mercury falls in the tube and a vacuum is formed above the mercury. The reason that all of the liquid mercury does not flow from the tube owing to gravitational attraction is that some is prevented from doing so by the pressure exerted by the atmosphere upon the surface of the mercury in the open vessel. The pressure exerted by the atmosphere is measured by the distance, *d*, between the level of the mercury in the tube and the level of the mercury in the open vessel. At sea level, the average pressure of the atmosphere is sufficient to support a column of mercury 760 mm. in height and is called *one atmosphere* (1 atm.). Accordingly, a pressure of 2 atm. would mean

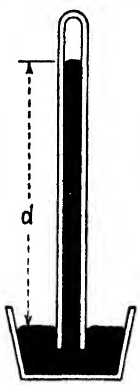


FIG. 16.—A simple type of barometer.

a pressure equal to that exerted by a column of mercury 1520 mm. in height, or twice the average pressure of the atmosphere at sea level.

5.5. Measurement of Volume

The unit of weight known as the *gram* has already been defined as the weight of one milliliter of water at 4°C. Accordingly, one kilogram (1000 g.) of water at 4°C. represents the weight of one *liter* of water. For purposes of comparison it is convenient to remember that the liter is a unit of volume just a little larger than the quart, since 1 liter = 1.0567 qt. In scientific work, relatively large volumes of liquids or solutions are expressed in terms of liters while smaller volumes are expressed in terms of *milliliters.* One milliliter is one one-thousandth part of a liter. The term *milliliter* is abbreviated as ml.

Another unit of volume which is commonly used, particularly in dealing with gases, is the *cubic centimeter* (abbreviated, cc.). A cubic centimeter is the volume enclosed by a cube one centimeter on an edge (inside measurement). Since 1 liter (1000 ml.) = 1000.028 cc., the two units, milliliter and cubic centimeter, are not identical. Although the difference between the two is so small as to be negligible for most purposes, the milliliter is most commonly used in expressing small volumes of liquids and solutions, while the two are used interchangeably in work involving small volumes of gases.

5.6. Relation between Pressure and Volume; Boyle's Law

If a definite quantity of a gas is confined at some fixed temperature in a cylinder fitted with a movable piston, the position of the piston will be such that the pressure exerted by the gas contained in the cylinder will be the same as that exerted by the outside atmosphere (Fig. 17). If now the outside pressure is increased to 2 atm., the piston will move downward in the cylinder until the confined gas occupies essentially one-half of the original volume. That is, if the pressure is doubled, the volume is decreased by one-half. Experiments of this kind led Robert Boyle, in the year 1660, to state what has come to be known as *Boyle's law.* **At constant temperature, the volume occupied by a definite weight of gas is inversely proportional to the pressure.** Or, stated in the form of a mathematical expression,

$$v \propto \frac{1}{p}$$

where v represents the volume and p represents the pressure. An *inverse* relationship such as this requires that, if one of two factors

changes in a given direction (*e.g.*, increases), the other factor must change to the same extent but in the opposite direction (*i.e.*, must decrease).

To replace the proportionality sign by an equality sign requires the introduction of a proportionality constant, k,

$$v = k\frac{1}{p}$$

or

$$pv = k$$

which is the usual mathematical expression of Boyle's law.

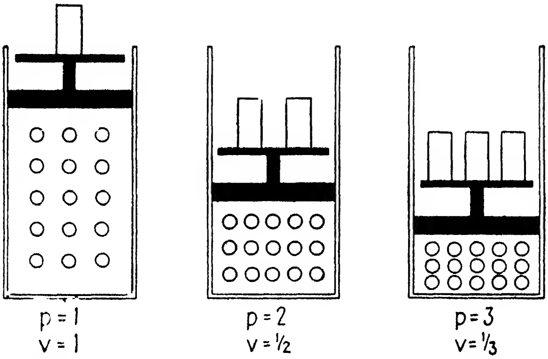


FIG. 17.—The relationship between the pressure exerted upon (or by) a confined gas and the volume which it occupies.

By reference to Fig. 17, Boyle's law may be explained in terms of the kinetic-molecular theory. In the first cylinder, the pressure exerted on the inner surface of the piston is the result of bombardment by the moving gas molecules contained in the cylinder and is the same as the pressure being exerted (in the same manner) by gas molecules of the atmosphere. When the external pressure is doubled and the piston assumes position B, the pressure exerted by the confined gas molecules must also be equal to 2 atm. The original number of gas molecules has been crowded into half the original space. Accordingly, the number of molecules per unit of volume has been doubled, the number of collisions per unit of time is doubled, and this results in a pressure twice as great as the original pressure.

Application of Boyle's Law. Suppose that a definite weight of oxygen gas occupies a volume of 593 cc. when under a pressure of 710 mm. at 25°C. In certain practical problems, it might be required to know the volume that this weight of gas would occupy if the pressure

was changed to 790 mm. and the temperature held constant. The answer to such a problem may be had readily by the application of Boyle's law. The volume, v_2, under the new conditions of pressure will be equal to the original volume, v_1, multiplied by a suitable fraction.

$$v_2 = v_1 \times (\text{a fraction})$$

This fraction may be looked upon as a correction factor which takes into account the change in pressure from $p_1 = 710$ mm. to the new pressure $p_2 = 790$ mm. The next question that arises is whether the fraction should be 710/790 or 790/710. To decide on this point requires only that one recall that, according to Boyle's law, an increase in pressure must result in a decrease in volume. Since it is proposed to *increase* the pressure from 710 to 790 mm., the new volume, v_2, must be less than the original volume, v_1, and the fraction used as the correction factor must be 710/790.

$$\begin{aligned} v_2 &= v_1 \times \frac{710}{790} \\ &= 593 \times \frac{710}{790} \\ &= 533 \text{ cc.} \end{aligned}$$

Other problems involving the application of Boyle's law are given in the exercises at the end of this chapter.

5.7. Relation between Volume and Temperature

When a gas is heated in a closed container so that the volume cannot change, the pressure exerted by the gas increases until the walls of the container are ruptured. If an overinflated automobile tire is driven over a hot highway, indisputable evidence of this increase in pressure may be experienced. There arises the question, however, as to how the volume ~~of a gas~~ will change with change in temperature if the gas is allowed to expand against a constant pressure. It has been found that for each degree change in the centigrade temperature, there is a change in volume equal to 1/273 of the volume at 0°C.

Absolute Temperature Scale. If a definite weight of a gas such as oxygen occupies a volume of 273 cc. at 0° and under a pressure of 1 atm. and the temperature is lowered to −1°C., the volume occupied by the gas at −1°C. would be 272 cc. (*i.e.*, a decrease in volume of 1/273 of the volume at 0°C.). With repeated lowering of the temperature, the volume will decrease in this same regular fashion as is shown by the following data:

When t = 0°C.,	v = 273 cc.
When t = −1°C.,	v = 272 cc.
When t = −2°C.,	v = 271 cc.
When t = −50°C.,	v = 223 cc.
When t = −150°C.,	v = 123 cc.
When t = −200°C.,	v = 73 cc.
When t = −273°C.,	v = ?

It appears from the above data that, if the temperature were lowered to −273°C., the volume would be *zero* and the gas would have disappeared. This, of course, could not occur (law of indestructibility of matter). Before such a temperature as −273°C. could be reached, the oxygen would become a liquid and then pass into the solid state. The temperature of −273°C. is known as the *absolute zero* since it is that temperature at which the volume occupied by a gas should, theoretically, become zero if gases were capable of existence at such a temperature.

The absolute (or Kelvin) temperature scale is based upon the absolute zero and is related to the centigrade scale as follows:

$$°A. = °C. + 273$$

To convert centigrade temperatures to the absolute scale, it is necessary only to add 273 to the centigrade temperature. It should be emphasized that the absolute temperature scale is not an arbitrary one; rather it is one that is directly based on the manner in which the volume of a gas varies with the change in temperature at constant pressure.

Charles' Law. An examination of the preceding data reveals that the volume occupied by a gas changes in a regular manner when the temperature is changed. Essentially the same regularity would have been observed had the temperature been increased rather than decreased and had some gas other than oxygen been used. This change in volume with change in pressure is described by Charles' law, which was first stated in 1801. **At constant pressure, the volume occupied by a definite weight of gas is directly proportional to the absolute temperature.** Since a direct proportionality is involved, if the temperature is doubled, the volume will also be doubled; if the temperature is halved, the volume must also be decreased to one-half the original volume. Stated mathematically, Charles' law becomes

$$v \propto t$$

and

$$v = kt$$

or

$$\frac{v}{t} = k$$

In terms of the kinetic-molecular theory, the pressure exerted by a gas depends upon the kinetic energy possessed by the molecules. If the temperature is increased, there is a corresponding increase in the kinetic energy of the gas molecules. As a result, they must move at greater velocities and consequently must strike exposed surfaces more frequently and with greater force. The gas expands against a constant pressure and occupies a volume which is related (by Charles' law) to the extent of the temperature increase.

Application of Charles' Law. If a given weight of oxygen gas occupies a volume of 616 cc. at a temperature of 25°C. and under a pressure of 750 mm., the extent to which the volume will change if the temperature is lowered to 10°C. and the pressure is not permitted to change may be calculated as follows. The volume, v_2, at the new temperature will be equal to the original volume, v_1, multiplied by a suitable fractional correction factor.

$$v_2 = v_1 \times \text{(a fraction)}$$

The correction factor, in fractional form, is concerned only with the two *absolute* temperatures, $t_1 = 25°\text{C.} + 273 = 298°\text{A.}$, and $t_2 = 10°\text{C.} + 273 = 283°\text{A.}$ According to Charles' law, if the temperature is *decreased*, the volume must also decrease and v_2, therefore, will be less than v_1. Accordingly, the fraction must be such that it will represent a number less than unity, *i.e.*, 283/298, and

$$\begin{aligned} v_2 &= v_1 \times \frac{283}{298} \\ &= 616 \times \frac{283}{298} \\ &= 585 \text{ cc.} \end{aligned}$$

5.8. Dalton's Law of Partial Pressures

Many experiments with gases are concerned with mixtures of different kinds of gases rather than with single pure gaseous substances. This raises the question as to the manner in which each gas in a mixture contributes to the total pressure exerted by the mixture. Suppose that a sample of pure oxygen gas is placed in a 1-liter flask (Fig. 18*a*) and exerts a pressure of 740 mm. and that a sample of pure nitrogen gas in a 1-liter flask also exerts a pressure of 740 mm. (Fig. 18*b*). If, now, the oxygen gas is forced into the flask containing the nitrogen (or vice versa) so that the two gases now occupy a total volume of 1 liter (Fig. 18*c*), the total pressure will be found to be 1480 mm. (*i.e.*, 740 + 740 mm.). In other words, each gas in the mixture behaves

just as though it were alone in the 1-liter flask and occupying the total volume of 1 liter. That part of the total pressure which is exerted by a given gas in a mixture is known as the *partial pressure* of that gas. The relation between total and partial pressures is described by Dalton's law. **The total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the various components.**

$$P_{(\text{total})} = p_a + p_b + p_c + \cdots$$

where p_a, p_b, p_c, etc., are the partial pressures of the different gases in the mixture.

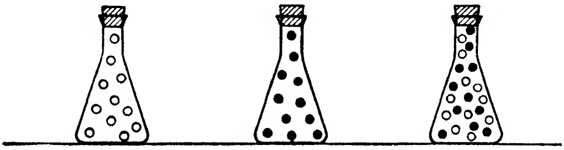


FIG. 18.—Illustration of Dalton's law of partial pressures.

5.9. Standard Conditions of Temperature and Pressure

From the foregoing discussion it is apparent that the volume occupied by a definite weight of gas has no real meaning unless the temperature and pressure are specified. In order to have a basis for the comparison of results of experiments which involve gases and which are conducted under different conditions of temperature and pressure, scientists have agreed to express gas volumes in terms of a *standard* set of conditions. The conditions agreed upon are a temperature of 0°C. (the melting temperature of ice) and a pressure of 760 mm. (the average pressure of the atmosphere at sea level). These are known as *standard conditions of temperature and pressure* and are commonly abbreviated S.T.P.

5.10. Experimental Measurement of Gas Volumes

In the laboratory, the volumes occupied by gases are usually measured by collecting and confining the gases over mercury, water, or some other suitable liquid. If a gas such as oxygen is collected over water (Fig. 19), the gas in the tube will consist of a mixture of oxygen and water vapor. The total volume of the mixture of gases contained in the tube may be read directly from the scale (usually in cubic centimeters) on the calibrated tube. When the level of the liquid in

the open container is the same as that of the liquid in the tube, the pressure exerted by the confined gas may be known simply by reading the barometer.

With the method illustrated by Fig. 19, 45 cc. of gas (oxygen + water vapor) were collected in a laboratory in which the temperature was 28°C. and the barometric pressure was 730 mm. The usual question that arises is, what volume will the *dry* oxygen gas occupy under standard conditions?

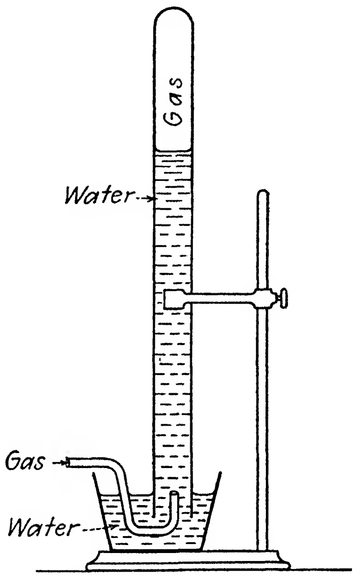


FIG. 19.—Collection of gases over water.

First, the total pressure P is, by Dalton's law, equal to the sum of the partial pressures of oxygen and water vapor.

$$p_{O_2} + p_{H_2O} = P_{(total)}$$
$$p_{O_2} = P_{(total)} - p_{H_2O}$$

In order to calculate the partial pressure of oxygen, it is necessary to know the partial pressure of water vapor. This information may always be obtained by referring to tables in which values for the vapor pressure[1] of water at different temperatures are listed as found by experiment (see Appendix). At 28°C., the partial pressure of water vapor is 28.3 mm., hence,

$$\begin{aligned} p_{O_2} &= P_{(total)} - 28.3 \\ &= 730 - 28.3 \end{aligned}$$

The volume under standard conditions, $V_{S.T.P.}$, will be equal to the measured volume after correction for the change in absolute temperature and the change in pressure.

$$\begin{aligned} V_{S.T.P.} &= 45 \times \frac{730 - 28.3}{760} \times \frac{0° + 273}{28° + 273} \\ &= 37.7 \text{ cc.} \end{aligned}$$

In this case, the fractional correction factors are set up on the same line of reasoning as was used in solving the problems used to illustrate separately the application of the laws of Boyle and Charles.

[1] See Sec. 6.5.

5.11. Diffusion of Gases

All our ideas concerning the nature of gases are based upon the assumption that gases consist of molecules in motion. That molecules do move (diffuse) through space can be demonstrated by numerous simple experiments. If two flasks, one containing oxygen and the other containing hydrogen, are placed mouth to mouth as shown in Fig. 20*a* and allowed to remain in this position, the molecules of hydrogen will move into the flask containing oxygen and the molecules of oxygen will move into the flask that originally contained only hydrogen (Fig. 20*b*). After sufficient time has elapsed, the two gases will be found to be uniformly distributed throughout the two flasks, as shown in Fig. 20*c*.

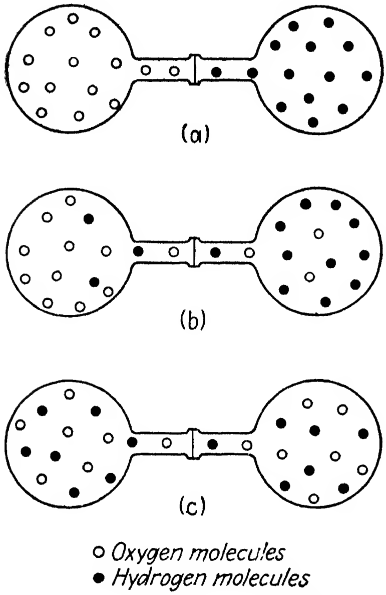


Fig. 20.—Illustration of diffusion of gases.

Density of Gases. Density is defined as the weight of matter contained in a specified unit of volume. The density of a gas must, of course, be specified in terms of the temperature and pressure (usually standard conditions). The units in which density is expressed may be grams per cubic centimeter, pounds per gallon, or any other convenient units. The densities of a few common gases are listed in Table 4.

TABLE 4
Absolute Density of Common Gases under Standard Conditions

Gas	Density, grams per liter
Hydrogen	0.0899
Oxygen	1.4290
Nitrogen	1.2505
Hydrogen chloride	1.6392
Ammonia	0.7710
Air	1.2930

The density values in Table 4 are *absolute* values. Chemists sometimes prefer to use *relative* density, which is the ratio of the weight of a given volume of a gas to the weight of an equal volume of air (arbi-

trarily chosen as a convenient standard). The relative density of hydrogen, for example, may be calculated as follows:

$$\text{Relative density of } H_2 = \frac{\text{absolute density of } H_2}{\text{absolute density of air}}$$
$$= \frac{0.0899}{1.2930}$$
$$= 0.0696$$

The relative densities of the gases listed in Table 4 are given in Table 5. Density should not be confused with *specific gravity* which is defined as the ratio of the weight of a given volume of a substance to the weight of an equal volume of water at the same temperature (usually 4°C.—the temperature at which water exhibits its maximum density).

TABLE 5

RELATIVE DENSITY OF COMMON GASES UNDER STANDARD CONDITIONS

Gas	Relative Density
Hydrogen	0.0696
Oxygen	1.1053
Nitrogen	0.9671
Hydrogen chloride	1.2677
Ammonia	0.5963
Air	1.0000

Rates of Diffusion; Graham's Law. If a heavy automobile and a light automobile were powered by the same kind of motor, the light car would of course be capable of traveling at the greater speed. Similarly, light molecules are capable of diffusing more rapidly than heavier molecules since the average kinetic energy of all kinds of gas molecules is the same. In 1832, Graham formulated a law to the effect that **the rate of diffusion of a gas is inversely proportional to the square root of its density.** If r represents the rate of diffusion and d represents the density, then,

$$r \propto \frac{1}{\sqrt{d}}$$

and

$$r = k\frac{1}{\sqrt{d}}$$

or

$$r\sqrt{d} = k$$

To provide some idea as to the absolute rate at which gas molecules move, it is of interest to note that hydrogen molecules (at ordinary temperatures) move at a rate of 1.14 *miles per second.*

Usually, chemists are interested not so much in the absolute rate at which a given gas will diffuse but rather in the relation between the rates of diffusion of two or more gases. In comparing, for example, the relative rates of diffusion of hydrogen and oxygen,

$$r_{H_2}\sqrt{d_{H_2}} = r_{O_2}\sqrt{d_{O_2}}$$

or

$$\frac{r_{H_2}}{r_{O_2}} = \frac{\sqrt{d_{O_2}}}{\sqrt{d_{H_2}}}$$

Since oxygen is sixteen times as heavy as hydrogen (1.4290/0.0899),

$$\frac{r_{H_2}}{r_{O_2}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

This means that, at the same temperature, hydrogen molecules diffuse four times as rapidly as oxygen molecules.

Demonstration of Rates of Diffusion. That hydrogen diffuses much more rapidly than ordinary air may be shown using an apparatus of the type shown in Fig. 21. *A* is a porous-walled porcelain cup containing air and connected by means of a glass tube to a bottle containing water. When the porous cup is surrounded by a bell jar filled with hydrogen, the hydrogen diffuses into the porous cup more rapidly than the air (oxygen and nitrogen) can diffuse out of the cup. This results in a positive pressure within the cup and, as a result, the water is forced out of the bottle *B* through the glass outlet tube.

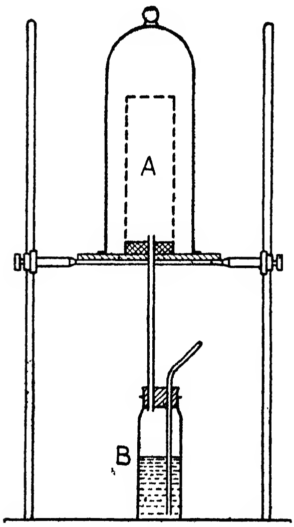


FIG. 21.—Apparatus for demonstration of diffusion of gases.

5.12. The Ideal Gas

No real gas such as oxygen or hydrogen behaves *strictly* in accordance with the mathematically exact gas laws. In their behavior toward changes in temperature and pressure, real gases deviate slightly from the gas laws. When the pressure on a given volume of oxygen is doubled, the volume is decreased almost but not quite exactly one-half. Chemists study the behavior of gases in terms of an imaginary *ideal gas* which, if such existed, would behave precisely as described by the laws of Boyle, Charles, etc. Real gases deviate from

the gas laws at ordinary pressures because of the attractive forces between molecules. The lower the pressure to which a gas is subjected, the farther apart are the molecules, and the more nearly does the behavior of a real gas approach that of the ideal or perfect gas. That is, real gases approach the behavior of the ideal gas only at very low pressures.

EXERCISES

1. Define the following terms: (*a*) barometer. (*b*) density, (*c*) absolute zero, (*d*) partial pressure, (*e*) relative density, (*f*) ideal gas.

2. Outline the essential ideas involved in the kinetic-molecular theory.

3. State each of the following laws in words and in the form of an exact mathematical expression: (*a*) Boyle's law, (*b*) Graham's law, (*c*) Dalton's law, (*d*) Charles' law.

4. Convert the following centigrade temperatures to the corresponding absolute temperatures: (*a*) 366°C., (*b*) −1°C., (*c*) −251°C.

5. Given the information that the absolute density of sulfur dioxide is 2.9269 g. per liter, calculate the relative density.

6. At a certain temperature, a sample of carbon dioxide gas occupied a volume of 871.5 cc. when under a pressure of 3 atm. If the temperature remains the same, what volume will the gas occupy if the pressure is decreased to 332 mm.?

7. When subjected to a pressure of 4263 mm. at 0°C., a certain quantity of helium gas occupies a volume of 3 cc. What pressure would be required to cause the same weight of helium to occupy a volume of 1250 cc. at 0°C.?

8. One hundred grams of a gas occupy a volume of 700 cc. at 25°C. under atmospheric pressure. Calculate the volume occupied by the same weight of the gas under atmospheric pressure at 5000°C.

9. The volume occupied by a sample of nitrogen gas at 100°C and 732 mm. is 510 liters. What volume will this gas occupy at a temperature of 273°A., if the pressure is held constant?

10. When collected over water in a laboratory in which the temperature was 30°C. and the barometric pressure was 695 mm., the gas obtained by heating a sample of mercuric oxide occupied a total volume of 82 cc. Calculate the volume of dry oxygen under standard conditions.

11. A sample of hydrogen was collected over water at 27°C. and 722 mm. and found to occupy a volume of 106 cc. Upon standing overnight, the temperature changed to 22°C. and the pressure increased to 753 mm. What volume did the gas occupy under these latter conditions?

12. (*a*) Three hundred twelve liters of ammonia gas were confined over mercury at 0°C. and 607 mm. pressure. What volume will this gas occupy under standard conditions? (NOTE: The partial pressure of mercury is so slight that it may be neglected.) (*b*) Calculate the weight of this particular sample of ammonia.

13. A mixture of gases consists of nitrogen, oxygen, and argon, and exerts a total pressure of 1.5 atm. If the partial pressure of oxygen is 427 mm., and the partial pressure of nitrogen is 531 mm., what is the partial pressure of argon?

14. Calculate the relative density of (*a*) nitrogen, (*b*) hydrogen chloride.

15. What weight of hydrogen would be required to fill a 10-liter flask at −15°C. and 740 mm.?

SUGGESTED READING

Journal of Chemical Education

CLARK, The Kinetic Theory, **1**, 75 (1924).

TIMM, The Kinetic-molecular Theory and Its Relation to Heat Phenomena, **12**, 31 (1935).

HAYS and GUSTAVSON, Simple Apparatus for Demonstrating Boyle's Law, **16**, 115 (1939).

WOLTHIUS, The Lowest Temperatures, **13**, 172 (1936).

ROSENBLUM, Upper Limit of Temperature, **17**, 438 (1940).

MEYER, The Solution of Gas Law Problems, **21**, 31 (1944).

CHAPTER VI

LIQUEFACTION OF GASES; PROPERTIES OF LIQUIDS AND SOLIDS

The relative simplicity of the structure of gases is due largely to the fact that gas molecules are normally so far apart that the forces of attraction between molecules cannot operate effectively against the kinetic energy that opposes these attractive forces. It is of interest, therefore, to inquire as to the changes that occur when the kinetic energy of gas molecules is decreased sufficiently to permit the attractive forces to assume a predominant role and to see whether the kinetic-molecular theory may be useful in explaining the nature of liquids and solids.

6.1. Liquefaction of Gases

In order to change a substance from the gaseous to the liquid state it is necessary that the gas molecules be brought so close together that the attractive force between them can operate to hold them in close proximity in the condition that is recognized as the liquid state. This may be accomplished by either of two methods, (*a*) by lowering the temperature, (*b*) by increasing the pressure, or by a combination of these two methods.

When the pressure is held constant and the temperature is progressively lowered, the kinetic energy of the gas molecules becomes less and less. Under these conditions, the volume decreases and the molecules move with diminished velocity and through shorter distances; the gas molecules are brought closer and closer together. If the gas is cooled sufficiently, the kinetic energy becomes so small that the force of attraction is capable of holding the molecules in clusters which first become visible in the form of a mist or fog. As these clusters of molecules become larger, drops of liquid appear. In this manner, any gas may be caused to pass from the gaseous to the liquid condition.

The molecules of a gas may also be brought together by subjecting the gas to increased pressure at constant temperature, *i.e.*, by compression. If sufficient pressure can be exerted upon the gas, the molecules may be forced into such limited space that they may be caused

to assume the liquid condition. There is, however, a serious limitation on the use of this method. For every gas there is a temperature above which that gas may not be liquefied by the application of pressure alone. This is known as the *critical temperature*. The critical temperatures of a few common gases are given in Table 6.

TABLE 6

CRITICAL TEMPERATURES OF GASES

Gas	Critical Temperature, °C.
Nitrogen	−147.1
Oxygen	−118.0
Carbon dioxide	31.35
Ammonia	132.4
Water	374.0

If the temperature of carbon dioxide gas, for example, is above 31.35°C., that gas cannot be liquefied by pressure alone no matter how great a

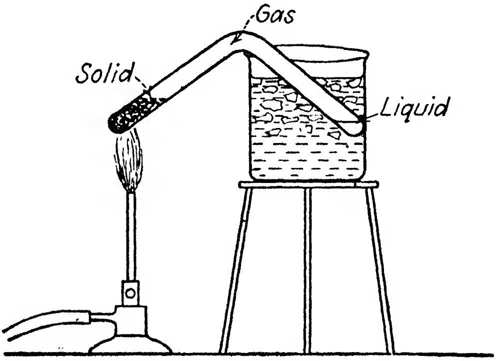


FIG. 22.—Liquefaction of a gas by the method of Faraday.

pressure might be exerted upon it. Above 31.35°, the kinetic energy of the carbon dioxide molecules is so great that they cannot be brought sufficiently close together solely by compression. The pressure necessary to liquefy a gas *at* its critical temperature is known as the *critical pressure*.

The combined effects of decrease in temperature and increase in pressure are illustrated by the liquefaction of ammonia, as shown in Fig. 22. A substance that, when heated, will liberate ammonia gas is placed in a bent glass tube and both ends of the tube are closed. One end of the tube is cooled in ice water. Ammonia is liberated as a gas by heating the solid in the other end of the tube. As the gas is liberated, the pressure within the tube increases and this, together with the cooling provided at one end of the tube, causes droplets of the liquefied gas to appear in the cold region of the tube.

6.2. Industrial Applications

The liquefaction of gases is an important commercial problem. Most of the gases produced and sold commercially are liquefied and stored in the liquid condition in heavy-walled steel cylinders. The industrial liquefaction of air (and other gases) employs the combined effects of cooling and compression. Advantage is taken of the fact that, when a cooled compressed gas is allowed to expand either with or without the performance of work, the gas becomes cooler.

Linde (or Hampson) Process. This process involves the expansion of cooled compressed gases without the performance of work and is best described by reference to Fig. 23. After partial removal of carbon dioxide and water vapor, the air to be liquefied enters at *B* and is compressed to about 200 atm. (3000 lb. per sq. in.) by the compressor

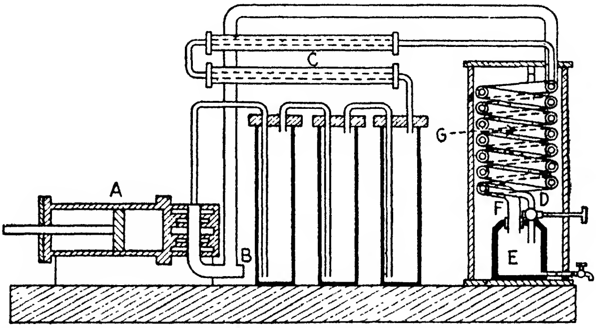


Fig. 23.—Diagram of equipment used in the liquefaction of air by the Linde process.

A. The warm compressed gas passes through the trap, driers, carbon dioxide removers, and the coolers *C*, and at *H* enters the inner tube of a dual concentric tube system *G*, which is efficiently insulated by means of sheep's wool, feathers, or balsa wood. By opening the valve *D* slightly the compressed gas is cooled considerably as it is allowed to expand into the chamber *E* to atmospheric pressure without doing any mechanical work. The cooled gas passes out of the chamber *E* at *F* into the outer tube of the dual system *G*, and this serves to lower the temperature of the incoming compressed gas in the inner tubes. When this cooled compressed incoming gas expands at *D*, the temperature falls still lower. If this cycle is operated for some time, the temperature continues to drop steadily within the entire cooling system until the gas liquefies in the receiving chamber *E*. For the liquefaction of air the required temperature is about $-190°C$.

The Claude Process. The fundamental principle underlying this process is again the effect of cooling; the cooling in this case, however,

is brought about by the utilization of the two effects, (1) the cooling effect due to expansion alone and (2) the cooling effect due to the performance of work. This process begins to differ from the Linde process at the point D in Fig. 23. Here, instead of allowing the gas to expand into a chamber at atmospheric pressure, the gas is caused to operate an air engine of the piston or turbine type. In so doing, the gas is cooled both by the expansion effect and by the work effect. The cooled gas is then sent through the outer coil F (as in the Linde process) and the entire cycle repeated until the temperature is lowered sufficiently to permit liquefaction of the gas. The efficiency of this process is much greater than that of the Linde process.

LIQUIDS

The transition from gas to liquid has been shown to result in a close packing of the molecules. Since the molecules in liquids are already practically touching one another, the space between them is so small that liquids cannot be made to occupy much smaller volumes by the application of pressure. That is, liquids cannot be compressed to any extent comparable to that possible in the case of gases. Despite their crowded condition, however, the molecules in a liquid are capable of motion although only through small distances and at relatively low velocities. So restricted is this motion that it may be described properly as a sort of vibration. If a colored liquid that is soluble in water is placed at the bottom of a tall glass cylinder filled with clear water, the molecules of the colored liquid will in time be seen to diffuse throughout the entire body of the liquid, thus proving that molecular motion is possible but relatively slow.

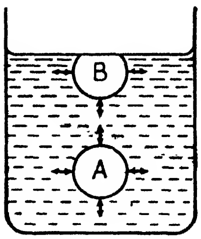


FIG. 24.—Illustration of surface tension of a liquid.

6.3. Surface Tension

Some insight into the properties of liquids may be had by considering the forces that influence molecules in different regions in the body of a liquid. A molecule in the interior of a liquid is surrounded on all sides by other molecules and is attracted equally in all directions, as shown in Fig. 24. Such a molecule, however, experiences no net restraint from these attractive forces and is restricted in its motion through the liquid because of the frequency with which it experiences collision. A molecule in the surface of the liquid is subject to an inequality of forces since there is no comparable attractive force directly above it. The attraction of the molecules in the body of the liquid tends to pull the molecule B into the body of the liquid. This force acting in an inward direction

causes a liquid to present the least possible exposed surface and is called the *surface tension*. It is because of the surface tension that individual drops of liquid tend to assume a spherical shape (for a given volume, the sphere presents the least possible surface), as is shown by Fig. 25. The surface tension is also responsible for the fact that liquids rise in capillary tubes, that oil rises in a lampwick, that objects can float on the surface of a liquid such as water, etc.

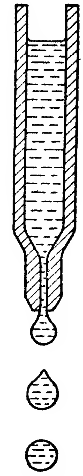


FIG. 25.—Effect of surface tension.

6.4. Viscosity

A property which is possessed by both gases and liquids (both of which are *fluids*) but which is far more pronounced in liquids is that known as *viscosity*, which may be defined as "resistance to flow." Liquids that have a high viscosity and show relatively little tendency to flow when their containers are inverted are said to be *thick*, *heavy*, or *viscous* liquids, *e.g.*, molasses, tar, etc.

The viscosity of liquids may be compared conveniently by measuring the time required for given volumes of different liquids to flow from the same small orifice (Fig. 26). The glass container is supported in a vertical position and filled with a liquid. As the liquid flows from the container, the time required for the surface of the liquid to move from A to B is measured. Similar measurements with different liquids make possible a direct comparison.

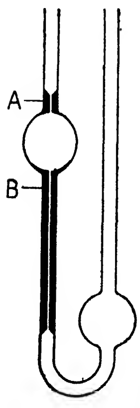


FIG. 26.—A convenient type of apparatus for measurement of the viscosity of a liquid.

The viscosity of a liquid depends upon the average velocity of the molecules, their size, and the distance between them. In the progress of liquid flow, these factors determine the ease with which molecules will roll over one another. The greater size of the molecules present in lubricating oil is largely responsible for the fact that the lubricating oil is much more viscous than gasoline, which contains relatively smaller molecules. That the viscosity of liquids decreases with increase in temperature is shown by the fact that lubricating oil becomes less viscous (thins out) at the operating temperature of a motor.

6.5. Vapor Pressure

Everyone is aware of the fact that, when water is allowed to stand exposed to the atmosphere, it will *evaporate*. Further, it is known that

water will evaporate more rapidly the drier the atmosphere and the higher the temperature. Aside from the temperature effect, the rate at which water molecules leave the liquid and enter the vapor state seems to depend upon the extent to which they are already present in the atmosphere.

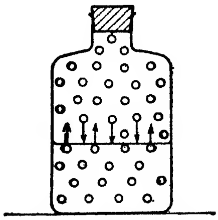


FIG. 27.—Equilibrium between liquid water, and water vapor.

If placed in a closed container at room temperature (Fig. 27), the water molecules will still pass into the atmosphere above the liquid but cannot continue to do so indefinitely, *i.e.*, not all of the water can evaporate. As more and more molecules enter the vapor state against the opposing pressure of the air above the liquid, some of them will in their motion through space strike the surface of and reenter the liquid. When the rate at which molecules return to the liquid is equal to the rate at which they are leaving the liquid, the two processes do not cease but continue to occur in opposite directions at the same rate.

$$H_2O_{(liquid)} \xrightarrow{\text{at rate } A} H_2O_{(vapor)}$$

$$H_2O_{(vapor)} \xrightarrow{\text{at rate } B} H_2O_{(liquid)}$$

$$\text{At equilibrium: rate } A = \text{rate } B$$

Thus is achieved a dynamic balance of opposing forces which is described as *dynamic equilibrium.* Under these conditions the space above the liquid is said to be *saturated* with water vapor. **The vapor pressure of a liquid is defined as the pressure exerted by the vapor upon the surface of the liquid when the two are in a condition of equilibrium.**

Some molecules in the body of a liquid are capable of escaping through the surface and into the vapor state because they have kinetic energies slightly greater than the average kinetic energy of all the molecules. With increase in temperature, the kinetic energy of all the molecules is increased. All liquids tend to evaporate, but at markedly different rates. At the same temperature, gasoline evaporates much more rapidly than water. A liquid that evaporates readily must have a high vapor pressure and is said to be *volatile.*

6.6. Boiling Temperature

When a liquid such as water is heated in an open container, the heat energy that is supplied to the water increases the kinetic energy of the water molecules and in this way serves to increase the rate of evapora-

tion. Since the water molecules leaving the surface of the liquid have increased kinetic energies, they are capable of doing work in pushing against the opposing atmospheric pressure. If the temperature of the water is increased sufficiently (to 100°C. at standard atmospheric pressure), the vapor pressure of the water becomes slightly greater than the opposing atmospheric pressure and the liquid is said to *boil.* The condition known as *boiling* is usually accompanied by the rise of bubbles of vapor from the body of the liquid. **The boiling temperature may be defined as the temperature at which the vapor pressure of a liquid just exceeds the opposing pressure of the atmosphere.** During the process of boiling, the heat supplied from the outside does not raise the temperature of the liquid but merely serves to accomplish the change in state from liquid to gas. The boiling temperature of a liquid is of course influenced by the magnitude of the opposing atmospheric pressure. At sea level, water boils at 100°C. while at the top of Mt. Everest (elevation about 29,000 ft. above sea level) water boils at 71°C. because the opposing pressure of the atmosphere is less at the higher altitude.

Although most liquids may be caused to boil at characteristically definite temperatures under normal conditions of pressure, some liquids decompose under the influence of heat before their boiling temperatures can be reached. Even certain of these, however, can be caused to boil without decomposition if the opposing atmospheric pressure is artificially lowered to a sufficient extent, thus enabling the liquids to boil at temperatures below their decomposition temperatures.

6.7. Freezing Temperature

Reference has been made in the preceding pages to the fact that liquid water changes to solid ice at 0°C. and that liquid oxygen solidifies at a temperature of −218.4°C. For most liquids there are characteristic and definite temperatures at which these liquids freeze or solidify. In most cases, when a liquid is cooled to its freezing temperature, solid *crystals* appear and at that temperature exist in equilibrium with the liquid. **The freezing temperature may be defined as that temperature at which the liquid and solid forms of a pure substance can exist together without change in temperature.** All liquids that solidify to form crystalline solids have definite freezing temperatures.

Manufacture of Ice. The principles employed in the commercial manufacture of ice are concerned with the fact that a gas is cooled by expansion and that the evaporation of a liquid withdraws heat from its surroundings. A combined ice-making and cold-storage sys-

tem is illustrated in Fig. 28. Ammonia gas is compressed by the pump *A* and is forced into the coils cooled by water sprayed from the pipe *B*. Under the combined effects of pressure and cooling, the ammonia liquefies and is forced through the valve *C* and into coils *F* immersed in brine. Here, the liquefied gas vaporizes and in so doing withdraws heat from the brine, thus lowering the temperature sufficiently to freeze the water contained in the ice tank *G*, which is also immersed in the brine. The gaseous ammonia is then returned to the compressor *A* and goes through the same cycle again and again. By pumping the cold brine (by means of the pump *D*) through the coils in the storage unit *E* at any desired rate, a low temperature may be maintained in the cold-storage compartment. Except for minor operative details, the same type of apparatus is employed in the small refrigera-

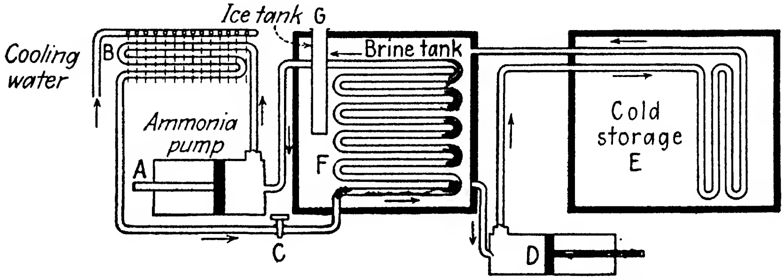


FIG. 28.—Combined ice-making and cold-storage system.

tion units used in the home. Gases other than ammonia may be employed. For example, sulfur dioxide (SO_2) and dichlorodifluoromethane or *Freon* (CCl_2F_2) are the gases most widely used in household refrigeration units.

SOLIDS

The conversion of a gas to a liquid has been seen to result in a profound restriction upon the motion of the molecules concerned. This restriction becomes still more pronounced when a liquid solidifies. The fixed physical form of solids and many other properties that characterize matter in the solid state are by-products of restricted molecular motion.

6.8. Melting Temperature[1]

When heat is supplied to a crystalline solid which is not decomposed by heat, the temperature of the solid is increased until sufficient to

[1] Temperatures of boiling, freezing, or melting are commonly referred to in a rather loose fashion as *points*. Thus, chemists speak of *boiling points*, *melting points*, etc.

cause the solid to *melt*. Further application of heat serves only to change the solid into the liquid condition. Obviously, the melting temperature of a pure solid such as ice is the same as the freezing or solidification temperature of the corresponding pure liquid (water) and is amenable to the same definition. The process of melting requires that the kinetic energy of the molecules of the solid be increased (by supplying energy in the form of heat) to such point that the molecules may be capable of motion to the extent normally possible in the liquid state.

6.9. Vapor Pressure

Some solids neither decompose nor melt when heated. Even at ordinary temperatures such solids have a pronounced tendency to evaporate. When the vapors come into contact with a cooled surface, they return directly to the solid condition. In Chap. 1 this change in state from solid to gas to solid was defined as *sublimation*, and solids that behave in this manner are said to *sublime*. Iodine, camphor, and "moth balls" [napthalene ($C_{10}H_8$) and paradichlorobenzene ($C_6H_4Cl_2$)] are common examples of solids that sublime readily. In all but a relatively small number of cases, the vapor pressure of solids is so small as to be negligible.

6.10. Crystalline Solids

The formation of a crystal upon solidification of a liquid requires that the molecules be arranged in *patterns of definite geometric form*

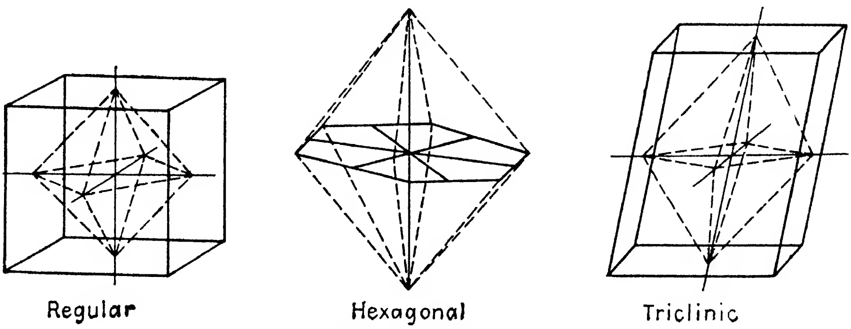
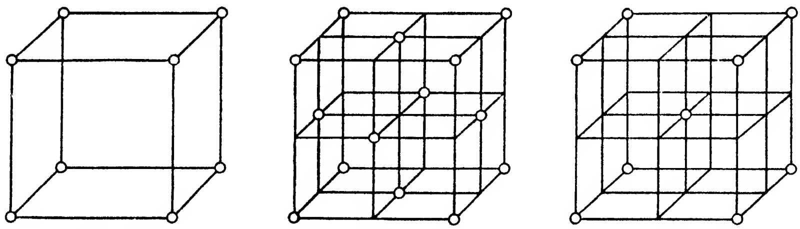


FIG. 29.—Crystal systems.

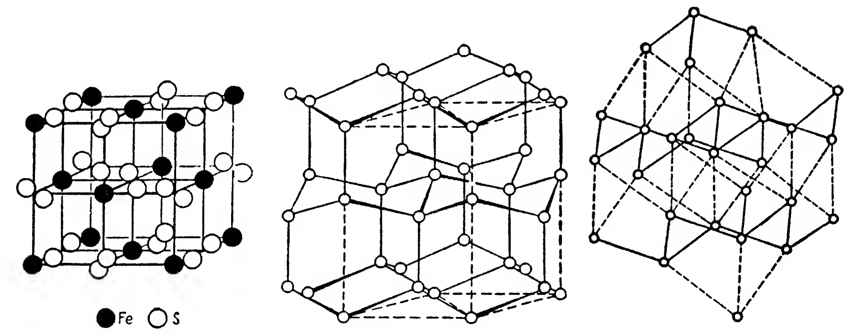
under the influence of forces of attraction or cohesion. With respect to each other, the molecules occupy essentially fixed positions in space, and molecular motion is possible only in an extremely small measure. Depending upon the type of crystal concerned, the units of matter that make up the crystal may be molecules, atoms, or *ions*. (Ions are atoms

or groups of atoms that have acquired either positive or negative electrical charges. The nature and origin of these charged particles will be discussed in a later chapter.)

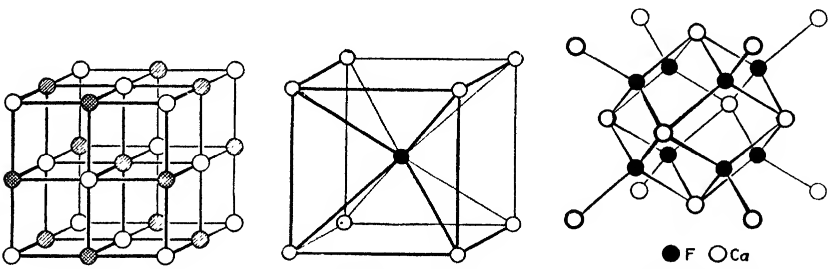


Simple cubic　　Face-centered cubic　　Body-centered cubic

FIG. 30.—Possible arrangements of structural units in the regular system.



Pyrite　　Mercury　　Bismuth



Sodium chloride　　Cesium chloride　　Calcium fluoride

FIG. 31.—The lattice structures of common crystals. (*Courtesy of Seitz, Modern Theory of Solids, McGraw-Hill Book Company, Inc.*)

The particular pattern in which the molecules, atoms, or ions are arranged within the crystal determines the *external form* of the whole crystal. The known forms or systems in which crystalline solids exist are six in number, three of which are illustrated in Fig. 29. Crystal-

line solids exhibit definite planes of cleavage and have definite melting temperatures.

Structure of Crystals. Present-day knowledge of the *internal structure* of crystals is the result of joint efforts of chemists and physicists. The experimental tool most useful in investigating the architecture of matter in the crystalline condition has been and is the X ray. By studying the manner in which X rays are reflected by crystals, much has been learned concerning the arrangement of the atoms, molecules, or ions with respect to one another. In the regular or cubic system (Fig. 29) the structural units may be arranged in the three patterns shown in Fig. 30. The structures of a number of common crystalline substances are shown in Fig. 31.

6.11. Amorphous Solids

Upon being cooled, some liquids fail to crystallize. They become more and more viscous until finally they exist in a solid condition. Pitch, tar, and glass are examples of such materials. These solids are described by the term *amorphous*, which is derived from the Greek word meaning "without form." Amorphous solids are characterized by the absence of any definite geometric arrangement of structural units and by the fact that they soften gradually upon being heated. They do not melt sharply at definite temperatures as do crystalline solids.

EXERCISES

1. Define the following terms: (*a*) critical temperature, (*b*) critical pressure, (*c*) surface tension, (*d*) viscosity, (*e*) vapor pressure, (*f*) dynamic equilibrium, (*g*) boiling temperature, (*h*) freezing temperature, (*i*) melting temperature.
2. What is meant by the expressions: (*a*) a volatile liquid, (*b*) a viscous liquid, (*c*) an amorphous solid, (*d*) a crystalline solid?
3. Why will a liquid boil at a lower temperature in a partial vacuum than at atmospheric pressure?
4. If a current of air is passed over the surface of a liquid, the rate of evaporation is increased. Explain.
5. What relationship exists between the vapor pressure of liquids and their boiling temperatures?

SUGGESTED READING

Journal of Chemical Education

CADY, Liquid Air, 8, 1027 (1931).
REINMUTH, Cooling and Refrigeration, 6, 1768 (1929).
DENUES, Liquid Oxygen Explosives, 18, 45 (1941).
EVANS, Refrigeration, 19, 539 (1942).

HAUSER, A Simple Method of Building Close-packed Molecular and Crystal Models, **18,** 164 (1941).

SEYMOUR, A Simple Method of Crystal Model Construction, **15,** 192 (1938).

HUGGINS, The Structure of Crystals, **4,** 73 (1927).

STILWELL, Crystal Chemistry, **10,** 590, 667 (1933); **11,** 159 (1934); **13,** 415, 469, 521, 566 (1936); **14,** 34, 131 (1937).

BROWN, The Atomic Arrangement in the Sulfur Unit Cell, **18,** 182 (1941).

CHAPTER VII

RELATIVE WEIGHTS OF MOLECULES

In Chap. I it was pointed out that the molecules of elemental gases, such as hydrogen, nitrogen, and chlorine, consist of 2 atoms each, H_2, N_2, Cl_2, etc. Since some information concerning the nature and behavior of gases in terms of the kinetic-molecular theory has been acquired, it now becomes possible to supply proof of the correctness of these formulas. The problem of deciding upon the number of atoms present in a given molecule is of course essentially the same as that involved in determining the relative weight of the particular molecule. If a hydrogen molecule contains 2 atoms, then the relative weight of the hydrogen molecule is 2.016 (*i.e.*, 2×1.008) based on the standard $O = 16$. But suppose that the number of atoms in the hydrogen molecule was unknown. This situation would require that the relative weight of the hydrogen molecule be determined by experiment in the laboratory. Methods are available whereby the molecular weights of both elemental and compound gases (as well as liquids and solids) may be measured by experiment.

7.1. Avogadro's Law

In 1811, the Italian physicist, Avogadro, voiced a prediction to the effect that **at the same temperature and pressure, equal volumes of all gases contain the same number of molecules.** At the time, Avogadro's prediction was perhaps nothing more than a reasonable supposition or guess. In subsequent years, however, the truth of this statement has been so firmly established that it has come to be known as Avogadro's *law.*

The far-reaching importance of Avogadro's law lies in the fact that it provides a concrete relationship between molecules (which are invisible) and the volumes that they occupy. While the scientist cannot work with individual molecules, he can manipulate definite volumes of gases which have real meaning in terms of the numbers of molecules present. A knowledge of the density of gases (Sec. 5.11) together with Avogadro's law makes possible a direct comparison of the weights of gaseous molecules.

Consider the volume occupied by a gas at standard conditions to be

1 liter, and represent the number of molecules by n. Since the density of hydrogen, for example, is known to be 0.0899 g. per liter at S.T.P., then the absolute weight in grams of the individual hydrogen molecule must be

$$\text{Wt. of 1 hydrogen molecule} = 0.0899 \div n$$

Similarly, from the known density of oxygen,

$$\text{Wt. of 1 oxygen molecule} = 1.4290 \div n$$

From this information, it is seen that the ratio of the weights of the individual molecules is

$$\frac{\text{Wt. of 1 oxygen molecule}}{\text{Wt. of 1 hydrogen molecule}} = \frac{1.4290 \div n}{0.0899 \div n} = \frac{1.4290}{0.0899} = \frac{15.88}{1}$$

This result is simply a *comparison* of the absolute weights of the molecules of oxygen and hydrogen and provides the information that the oxygen molecule is 15.88 times as heavy as the hydrogen molecule.

Since the relative weights of atoms are based on the arbitrarily selected standard of O = 16, the relative weights of molecules should be expressed on the same basis. If the number of atoms in either the hydrogen or oxygen molecule were known, then the foregoing ratio could be used to calculate the molecular weight of the other.

7.2. Gay-Lussac's Law

Three years before the first enunciation of Avogadro's law, Gay-Lussac observed that there is a simple relationship between the volumes

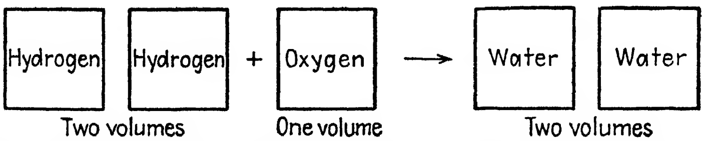


FIG. 32.—Combining volumes: formation of water from hydrogen and oxygen.

of gases that combine in or are produced by chemical reactions. For example, at the same temperature and pressure, two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapor (Fig. 32). Similarly, when solid sulfur is burned in oxygen, one volume of oxygen produces one volume of sulfur dioxide (Fig. 33). One volume of hydrogen and one volume of chlorine unite to form two

volumes of hydrogen chloride (Fig. 34), and three volumes of hydrogen and one volume of nitrogen combine to form two volumes of ammonia (Fig. 35). From many such observations, Gay-Lussac formulated a law to the effect that **at the same temperature and pressure, the ratio by volume in which gases combine in or are produced by chemical reactions may be expressed by small whole numbers.**

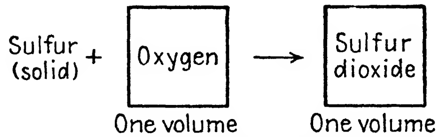


FIG. 33.—Combining volumes: formation of sulfur dioxide from sulfur and oxygen.

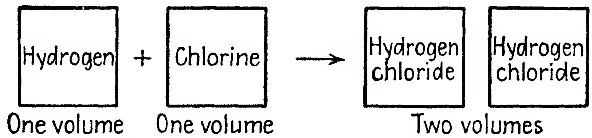


FIG. 34.—Combining volumes: formation of hydrogen chloride from hydrogen and chlorine.

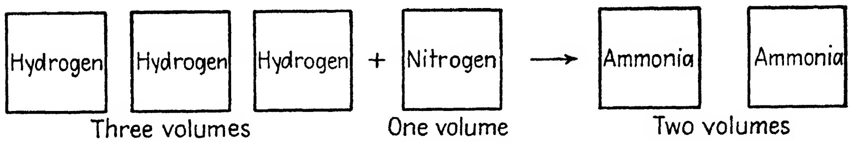


FIG. 35.—Combining volumes: formation of ammonia from hydrogen and nitrogen.

Thus, the ratios of the volumes of gases concerned in the reactions illustrated by Figs. 32 to 35, may be expressed as

$$\begin{aligned} \text{Hydrogen:oxygen:water vapor} &= 2:1:2 \\ \text{Oxygen:sulfur dioxide} &= 1:1 \\ \text{Hydrogen:chlorine:hydrogen chloride} &= 1:1:2 \\ \text{Hydrogen:nitrogen:ammonia} &= 3:1:2 \end{aligned}$$

Together, the laws of Avogadro and Gay-Lussac make possible the proof of the statement that the molecules of some elemental gases contain at least 2 atoms each.

7.3. Composition of Simple Gas Molecules

By reference to Fig. 34, it is seen that one volume of hydrogen and one volume of chlorine combine to form two volumes of hydrogen chloride. At the same temperature and pressure, each of these volumes must (according to Avogadro's law) contain the same number of molecules. If it is assumed that these volumes are of such size that

each contains exactly 1000 molecules, then the reaction may be represented as shown in Fig. 36. Attention must now be focused on the 2000 molecules of hydrogen chloride. Since hydrogen chloride is a compound containing hydrogen, each individual molecule of it must contain some hydrogen. The smallest "piece" of hydrogen that can be present in a molecule of any compound must be an *atom* of hydrogen (see definition of the term *atom*, Sec. 1.12). Therefore, the 2000 molecules of hydrogen chloride must contain *at least* 2000 atoms of hydrogen. *The* 2000 *atoms of hydrogen had to come from only* 1000 *molecules of hydrogen.* The inescapable conclusion is that each of the 1000 molecules of hydrogen must have contained at least 2 atoms.

The same line of reasoning may be applied in the case of chlorine, or in the case of reactions involving other simple gases. This procedure does not in itself prove that the number of atoms in these mole-

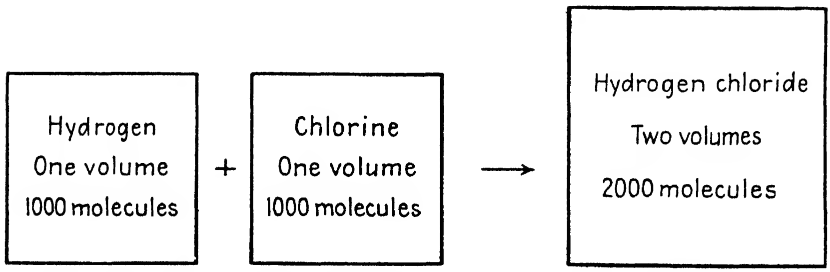


FIG. 36.—Diagram illustrating relationships involved in the proof of the diatomic nature of simple gas molecules.

cules may not be greater than two, but it does prove that the number must be *at least* two. By a variety of experimental methods, which need not be discussed here, the correctness of the number two has been firmly established.

7.4. Molecular Weight of Oxygen

In the preceding section it was concluded that the hydrogen molecule contains 2 atoms. On the scale of relative atomic weights already established, the relative weight of the hydrogen atom is 1.008. Consequently, the relative weight of the hydrogen molecule must be 2×1.008 or 2.016.

In Sec. 7.1, Avogadro's law was used to show that the oxygen molecule is 15.88 times as heavy as the hydrogen molecule. Hence, the relative weight of the oxygen molecule must be 15.88×2.016, or 32. The correctness of this result may be confirmed by (1) direct measurement of the molecular weight of oxygen by suitable laboratory experiments and (2) proving (by the method outlined in Sec. 7.3) that

the oxygen molecule contains at least 2 atoms and recalling that the relative atomic weight of oxygen is 16.

7.5. Determination of Molecular Weights by Experiment

Calculation of the ratios of the molecular weights of gases has shown that, at the same temperature and pressure, the molecular weights of different gases bear to each other the same relationship as exists between the weights of equal volumes of the gases. If, then, the weight of a known volume of a gas is determined (by direct weighing) in the laboratory, the molecular weight of the gas may be calculated in relation to the weight of the same volume of a gas of known molecular weight.

Suppose, for example, that 55.3 cc. of pure dry nitrogen is weighed by means of an accurate balance and found to weigh 0.0625 g. in a laboratory in which the temperature is 26°C. and the barometric pressure is 752 mm. Under standard conditions, this weight of nitrogen will occupy a volume given by

$$\begin{aligned} V_{\text{at S.T.P.}} &= 55.3 \times {}^{273}\!/_{299} \times {}^{752}\!/_{760} \\ &= 50 \text{ cc.} \end{aligned}$$

If 50 cc. of nitrogen at S.T.P. weighs 0.0625 g., then 1 liter of the gas will weigh 1.2505 g. under the same conditions.

$$0.0625 \times {}^{1000}\!/_{50} = 1.2505 \text{ g.}$$

One liter of hydrogen (molecular weight = 2.016) at S.T.P. weighs 0.0899 g. Therefore,

$$\frac{\text{Mol. wt. of nitrogen}}{\text{Mol. wt. of hydrogen}} = \frac{\text{wt. of 1 liter of nitrogen}}{\text{wt. of 1 liter of hydrogen}}$$

Substituting,

$$\frac{\text{Mol. wt. of nitrogen}}{2.016} = \frac{1.2505}{0.0899}$$

$$\begin{aligned} \text{Mol. wt. of nitrogen} &= 2.016 \times \frac{1.2505}{0.0899} \\ &= 28 \end{aligned}$$

This experimental result is confirmed when it is recalled that the molecule of nitrogen contains 2 atoms, each having a weight of 14 units in relation to O = 16.

Molecular Weights of Compound Gases. The discussion and examples previously given have been restricted to elemental gases. That the molecular weights of compound gases may be calculated from

experimental data in the same manner is shown by the following example. By a similar experiment, a known volume of sulfur dioxide gas was found to weigh 0.07428 g. Corrected to standard conditions, this sample occupied a volume of 26 cc., from which it was calculated that 1 liter of sulfur dioxide gas at S.T.P. weighs 2.8572 g. The molecular weight of sulfur dioxide is given by

$$\frac{\text{Mol. wt. of sulfur dioxide}}{2.016} = \frac{2.8572}{0.0899}$$

$$\begin{aligned}\text{Mol. wt. of sulfur dioxide} &= 2.016 \times \frac{2.8572}{0.0899} \\ &= 64\end{aligned}$$

At this point it might appear to the student that all of this is unnecessary. After all, sulfur dioxide has the formula SO_2, the atomic weight of sulfur is 32, that of oxygen is 16, and it follows that the molecular weight of sulfur dioxide is $32 + (2 \times 16) = 64$. But suppose that, as is often the case, the true formula is not known. Compounds hitherto unknown in the experience of man are discovered in the laboratory every day. The following outline of a typical situation will serve to establish the need for methods that permit the calculation of molecular weights from experimental data.

A new chemical compound was produced in the laboratory and found by qualitative analysis to contain only the elements of carbon and hydrogen. Quantitative analysis showed that this compound consisted of 82.76 per cent of carbon and 17.24 per cent of hydrogen. From this information, the simplest formula was shown to be C_2H_5, *i.e.*, carbon atoms and hydrogen atoms were shown to be present in the ratio of 2 to 5. But this same ratio is maintained in all the compounds having the formulas (and molecular weights) listed below.

Compound	Mol. wt.	C/H ratio
C_2H_5	29	$2/5$
C_4H_{10}	58	$2/5$
C_6H_{15}	87	$2/5$
C_8H_{20}	116	$2/5$

Obviously, a knowledge of the molecular weight of the new compound is required before a decision as to the correct formula can be made. By the method previously described, this particular compound was found to have a molecular weight of 58, from which it followed that the correct formula was C_4H_{10}.

7.6. Gram-molecular Volume

Knowing the densities and molecular weights of a number of simple and compound gases, it becomes of interest to calculate the volume which, at standard conditions, will contain *exactly one gram-molecular weight of each gas.* The data necessary for such calculations are assembled in Table 7.

TABLE 7
DENSITIES AND GRAM-MOLECULAR WEIGHTS OF SOME COMMON GASES

Gas	Mol. wt.	Density, grams per liter at S.T.P.
Hydrogen (H_2)	2.016	0.0899
Methane (CH_4)	16.031	0.7168
Ammonia (NH_3)	17.031	0.7710
Nitrogen (N_2)	28.016	1.2505
Hydrogen sulfide (H_2S)	34.016	1.5390
Chlorine (Cl_2)	70.914	3.2140

If 0.0899 g. of hydrogen occupies a volume of 1000 cc. at S.T.P., then the volume that will be occupied by 2.016 g. of hydrogen under the same conditions of temperature and pressure is

$$\frac{V}{2.016} = \frac{1000}{0.0899}$$

$$V = \frac{1000 \times 2.016}{0.0899}$$

$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

Thus, if one should fill a container of 22.4 liters volume with hydrogen at 0° and 760 mm., there would be contained therein exactly 1 gram-molecular weight of hydrogen.

Similar calculations, in abbreviated form, are given below for each of the other five gases listed in Table 7.

For methane:
$$V = \frac{1000 \times 16.031}{0.7168}$$
$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

For ammonia:
$$V = \frac{1000 \times 17.031}{0.7710}$$
$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

For nitrogen:
$$V = \frac{1000 \times 28.016}{1.2505}$$
$$= 22{,}400 \text{ cc., or } 22.4 \text{ liters}$$

For hydrogen sulfide: $V = \dfrac{1000 \times 34.016}{1.5390}$

$= 22{,}400$ cc., or 22.4 liters

For chlorine: $V = \dfrac{1000 \times 70.914}{3.2140}$

$= 22{,}400$ cc., or 22.4 liters

This striking result is not accidental. The gases for which these calculations are made were chosen at random, and this list of gases and the corresponding calculations could be extended indefinitely, always with the same result.

This volume of 22.4 liters is known as the **gram-molecular volume** and is commonly abbreviated as G.M.V. It is that volume

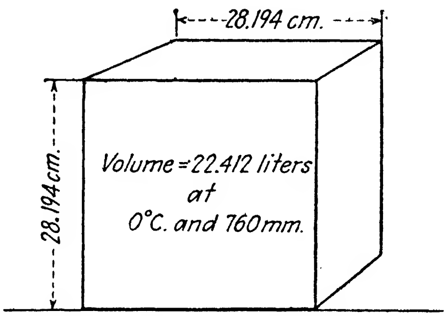


FIG. 37.—The gram-molecular volume.

which under standard conditions will contain exactly 1 gram-molecular weight of any gas, either elemental or compound. The volume of 22.4 liters is approximately ¾ cu. ft. and is represented exactly (Fig. 37) by a cube with 28.194 cm. edge (inside measurement).

7.7. Use of the Gram-molecular Volume in the Solving of Practical Problems

The gram-molecular volume is a perfectly definite relationship between weight and volume. Through its use, the chemist solves with ease many problems which are frequently encountered in practical applications of chemistry and which might otherwise be more difficult or at least more time-consuming.

Calculation of Molecular Weights. In Sec. 7.5, there was outlined for the calculation of molecular weights a method that depended upon a comparison with the weight of an equal volume of another gas of known molecular weight. By this method, the molecular weights of nitrogen and sulfur dioxide were calculated by using hydrogen as a

reference substance. Although this method is perfectly sound, it does require that one remember (or look up in handbooks where such data are tabulated) the weight of 1 liter or the weight of some other definite volume of hydrogen.

In Sec. 7.5, it was shown that a given sample of nitrogen weighs 0.0625 g. and occupies a volume of 50 cc. at S.T.P. This information together with the gram-molecular volume is all the information required to calculate the weight of nitrogen contained in 22.4 liters, which weight is, of course, the gram-molecular weight of nitrogen.

$$\frac{\text{Mol. wt. of nitrogen}}{22{,}400 \text{ cc.}} = \frac{0.0625}{50}$$

$$\begin{aligned}\text{Mol. wt. of nitrogen} &= \frac{0.0625 \times 22{,}400}{50} \\ &= 28\end{aligned}$$

In a similar manner, the molecular weight of the compound gas, sulfur dioxide, is calculated. If at S.T.P., 0.07428 g. of sulfur dioxide occupies a volume of 26 cc., then the molecular weight of this gas is given by

$$\begin{aligned}\text{Mol. wt. of sulfur dioxide} &= \frac{0.07428 \times 22{,}400}{26} \\ &= 64\end{aligned}$$

Calculation of Weight of a Gas Contained in Any Specified Volume under Any Experimental Conditions. For use in a given experiment, a chemist needed 2000 g. of hydrogen sulfide gas. The only hydrogen sulfide that was available was that contained in a 150-liter tank at a pressure of 10 atm. and at 30°C. The question was whether the *weight* of hydrogen sulfide in the tank was sufficient for the experiment.

The answer to this question may be had by the use of the gram-molecular volume relationship. At S.T.P., the hydrogen sulfide contained in this tank would occupy a volume of

$$\begin{aligned}V_{\text{at S.T.P.}} &= 150 \times \frac{273}{303} \times \frac{10 \times 760}{760} \\ &= 1{,}350 \text{ liters}\end{aligned}$$

But 22.4 liters of hydrogen sulfide (at S.T.P.) weighs 34.016 g. (the gram-molecular weight of hydrogen sulfide). The weight of H_2S in the tank is therefore readily calculated as follows:

$$\frac{\text{Wt. of } H_2S}{1350} = \frac{34.016}{22.4}$$

$$\text{Wt. of } H_2S = 1350 \times \frac{34.016}{22.4}$$

$$= 2050 \text{ g.}$$

or 50 g. in excess of the required amount.

To consider another example, assume that, in order to calculate the relative density of the gas known as phosphine (PH_3), it is convenient to know the weight of 1 liter of this gas at S.T.P. The molecular weight of phosphine is 34.024, which is the weight contained in 22.4 liters of PH_3 at S.T.P. Hence,

$$\text{Wt. of 1 liter of } PH_3 = \frac{34.024}{22.4}$$

$$= 1.5189 \text{ g.}$$

Calculation of Volumes of Gases Consumed in or Produced by Chemical Reactions. The union of iron and oxygen may be represented by the following equation:

$$4Fe + 3\overline{O}_2 \rightarrow 2Fe_2O_3$$

If one wished to know the *volume* of oxygen required to burn a given quantity of iron, the *weight* of oxygen could be calculated and divided by the weight of 1 liter of oxygen to find the volume required. However, a simpler procedure is now available. The equation provides the information that the burning of 4 gram atoms of iron

$$(4 \times 55.84 = 223.36 \text{ g.})$$

requires 3 gram-molecular volumes of oxygen ($3 \times 22.4 = 67.2$ liters) at S.T.P. Hence, the volume of oxygen required to burn, for example, 266 g. of iron may be calculated as follows:

$$\frac{\text{Vol. of } O_2}{266} = \frac{67.2}{223.36}$$

$$\text{Vol. of } O_2 = 266 \times \frac{67.2}{223.36}$$

$$= 80 \text{ liters}$$

With the volume at S.T.P. known to be 80 liters, the volume under any other conditions of temperature and pressure may be calculated by application of the laws of Boyle and Charles.

Problems based on equations and involving gases may be solved directly in terms of volume by the application of the gram-molecular volume relationship.

7.8. Molecular Weights of Liquids and Solids

The methods discussed thus far are suitable only for the determination of the molecular weights of gases. The same methods may be used in the case of liquids and solids that are volatile. All that one need do is to volatilize a sample of the liquid or solid and determine the weight of a known volume of the vapor at any convenient temperature and pressure. From these data, as has already been demonstrated, the molecular weight may be calculated. There are many liquids and solids, however, whose molecules undergo change with change in physical state. Still others are essentially nonvolatile. In these instances, it is necessary to resort to other methods such as those based upon a knowledge of the properties of solutions.

7.9. Avogadro Number

On two occasions (Secs. 2.8, 2.9) reference has been made to that number which represents (1) the number of atoms in 1 gram-atomic weight of an element and (2) the number of molecules in 1 gram-molecular weight (or gram-molecular volume) of an elemental or compound substance. This number, 6.02×10^{23} (the Avogadro number), has been determined *experimentally* by a wide variety of independent methods. The value generally accepted as being the most accurate is that given above.

EXERCISES

1. Distinguish clearly between absolute and relative weights of molecules.

2. State (*a*) Avogadro's law, (*b*) Gay-Lussac's law.

3. Using the reaction between nitrogen and hydrogen (Fig. 35), develop an argument leading to the conclusion that the nitrogen molecule contains 2 atoms.

4. On the basis of Avogadro's law, show that the chlorine molecule is two times as heavy as the molecule of hydrogen sulfide.

5. A 38-cc. sample of a certain gas at 23°C. and 774 mm. weighs 0.0937 g.

(*a*) Calculate the molecular weight of this gas using hydrogen as a reference substance.

(*b*) Make the same calculation using nitrogen as the reference substance.

(*c*) Calculate the molecular weight of this gas through use of the gram-molecular volume relationship.

6. A gaseous compound contains carbon and hydrogen only, the ratio C/H being 12/1. At 100°C. and 760 mm., 1 liter of the gas weighs 0.8491 g. What is the true formula for this substance?

7. What volume will be occupied by 1 g. of acetone (C_3H_6O) in the vapor state at 75°C. and 2 atm. pressure?

8. How many liters of oxygen may be collected over mercury at 30°C. and 758 mm. by complete decomposition of 200 g. of $KClO_3$?

9. Nitrogen gas is stored at 20°C. and 6 atm. in a steel cylinder having a

capacity of 41.32 liters. What weight of nitrogen is contained in the cylinder under these conditions?

10. The weight of 0.5 cc. of a certain gas at S.T.P. is 0.00198 g. Calculate the molecular weight of this gas.

11. A gaseous compound has the formula SiH_4. What is the weight of 110 cc. of this gas at 25°C. and 750 mm.?

SUGGESTED READING

See references at the end of Chap. II.

CHAPTER VIII

PREPARATION AND PROPERTIES OF HYDROGEN; RELATIVE ACTIVITY OF METALS

Hydrogen occupies a unique position among the elements in that it is the lightest known elemental substance. It occurs on the earth in tremendous quantities in combination with other elements and in like quantity (but in the uncombined condition) in the atmosphere of the sun. In 1766, Cavendish prepared hydrogen by a number of methods and studied many of its properties. He called it *inflammable air* and apparently failed to recognize it as an element. Somewhat later Lavoisier showed that this gas is one of the components of water and gave it the name *hydrogen* which means "water former."

A detailed study of the chemical and physical properties of hydrogen is appropriate at this juncture since certain important generalizations depend upon the relationship between hydrogen and the other elements. For example, the ability of the elements to hold each other in chemical combination may be expressed in relation to hydrogen.

8.1. Laboratory Methods for the Preparation of Hydrogen

There are three convenient methods by means of which hydrogen is usually prepared for small-scale laboratory use. Each of these methods will be considered in some detail.

Preparation from Metals and Acids. Acids are substances that consist of hydrogen combined with one or more nonmetals, *e.g.*, hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). When certain acids are allowed to react with certain of the metals, hydrogen gas is liberated and there are formed also compounds known as *salts*. In these salts, the metals are found to be combined with the nonmetals which were originally combined with hydrogen in the acid used. Reactions that serve to illustrate this method of preparation are represented by the following equations:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

$$2Na + 2HCl \rightarrow 2NaCl + H_2$$

$$\underset{\text{Phosphoric acid}}{2Al + 2H_3PO_4} \rightarrow 2AlPO_4 + 3H_2$$

$$\underset{\text{Acetic acid}}{Mg + 2HC_2H_3O_2} \rightarrow Mg(C_2H_3O_2)_2 + H_2$$

Not all acids may be used in the preparation of hydrogen. Nitric acid and *concentrated* sulfuric acid react with metals to form salts and products other than hydrogen. Neither may all metals be used. Some metals react with acids so slowly that their use would be inadvisable; other metals are incapable of reaction with acids. Zinc and hydrochloric acid or dilute sulfuric acid are the substances most often employed in the laboratory for the preparation of hydrogen (Fig. 38).

With any given acid, the reactions with different metals do not all occur at the same rate. Some metals react vigorously, others

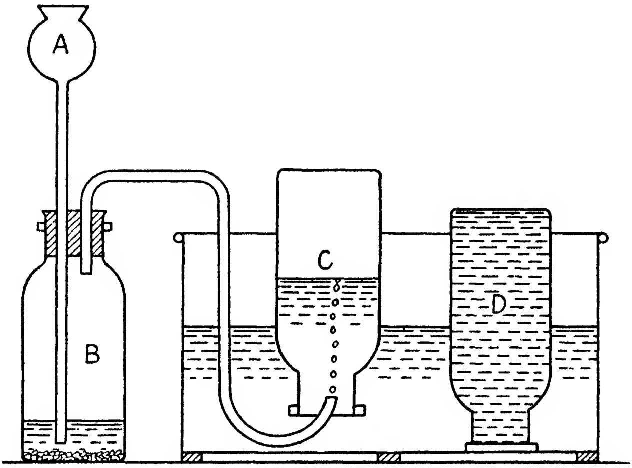


FIG. 38.—Convenient laboratory apparatus for the preparation and collection of hydrogen gas. Acid is added through the thistle tube, *A*, to the metal contained in bottle *B*. The hydrogen liberated is collected by displacement of water contained in bottles *C* and *D*.

somewhat more slowly, and still others react only extremely slowly or not at all.

Preparation from Metals and Water. Just as certain metals are capable of displacing the hydrogen from certain acids, so hydrogen may be displaced from water under suitable conditions. At ordinary temperatures, the metal sodium displaces hydrogen from cold water in a reaction that is extremely vigorous.

$$2Na + 2HOH \rightarrow 2NaOH + H_2$$

The other product in reactions of this type is known as a *base* and consists of a metal in combination with hydrogen and oxygen.

If the metal magnesium is allowed to react with cold water, the reaction is very slow. With hot water, however, hydrogen is liberated at an appreciable rate.

$$Mg + 2HOH \rightarrow Mg(OH)_2 + H_2$$

The metal iron does not react either with cold or hot water at an appreciable rate. With steam, the reaction proceeds at a rate such that this may be used in the laboratory preparation (or commercial production) of hydrogen.

$$3Fe + 4HOH \rightarrow Fe_3O_4 + 4H_2\uparrow$$

In this particular reaction, an oxide and not an hydroxide is formed as a by-product.

It should be emphasized that all metals do not react with water and that those which react do so at markedly different rates.

Preparation from Metals and Bases. A few of the metals such as aluminum and zinc react with bases with liberation of hydrogen accompanied by the formation of salts.

$$Zn + 2NaOH \rightarrow (NaO)_2Zn + H_2\uparrow$$
$$2Al + 6NaOH \rightarrow 2(NaO)_3Al + 3H_2\uparrow$$

Here, as before, the reactions are of the same general character but occur at different rates. Of the three methods for the preparation of hydrogen, the action of bases on metals is the least used.

8.2. Order of Activity of Metals

When the reactions of a large number of metals with (1) acids, (2) water, (3) bases, (4) oxygen, (5) other elements, and (6) other compounds are investigated in the laboratory, it is found that the various metals react at different rates. That is, these metals seem to exhibit different tendencies toward participation in chemical changes. Measurement of the rates at which metals react with various substances (*e.g.*, acids) makes possible the establishment of a definite "order of activity" such as that given in Table 8. In this table the metals are listed in *decreasing* order of activity, *i.e.*, the higher the metal in this series the greater is its activity or tendency to react. For the sake of simplicity many of the less common metals have been omitted, but such a list could be established readily to include all the known metals.

TABLE 8
ORDER OF ACTIVITY OF METALS

Potassium
Barium
Calcium
Sodium
Magnesium
Aluminum
Manganese
Zinc
Chromium
Iron
Cadmium
Nickel
Tin
Lead
Hydrogen
Bismuth
Copper
Silver
Mercury
Platinum
Gold

The inclusion of hydrogen (a nonmetal) is worthy of particular attention. Even if there were no better reason, its inclusion could easily be justified because in its reactions hydrogen exhibits many similarities to the metals. Hydrogen is included also because it provides a line of demarkation between those metals which will and those metals which will not react with acids to liberate hydrogen. In this connection, the following generalizations may be made:

1. Metals above hydrogen react with acids (other than ones such as nitric and concentrated sulfuric) to form hydrogen and a salt. Furthermore, the farther a metal stands above hydrogen, the more vigorous is its reaction with an acid.
2. Metals below hydrogen do not react with acids with liberation of hydrogen.
3. The metals below hydrogen and above platinum react with acids such as nitric and concentrated sulfuric to form salts and products other than hydrogen.
4. Platinum and gold do not react with acids of any kind.

8.3. Radicals

The equations written to represent the reactions by means of which hydrogen may be prepared present some problems not previously encountered by the beginning student. In the equation,

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

A portion, SO_4, of the formula for the acid is also a part of the formula for the salt ($ZnSO_4$). It appears that this particular group of atoms was unaltered in the course of the reaction. Inspection of the other equations reveals the presence of several groups of atoms which behave similarly, *e.g.*, PO_4, $C_2H_3O_2$, OH, and NaO. Such groups of atoms are known as *radicals*. **A radical is defined as a group of atoms that behaves as an unaltered unit in a chemical reaction.** Where different radicals or two or more of the same kind of radical are present in the formula of a compound, these radicals are usually enclosed in parentheses. It should not be inferred that a group of atoms that constitutes a radical in one reaction must always behave as a unit. All the common radicals can be disrupted by suitable kinds of chemical attack.

8.4. Valence

Another problem involved in the writing of equations of the type given in Sec. 8.1 has to do with the ability of the metals to displace hydrogen from its compounds. A careful inspection of these equations

leads to the conclusion that some metals can displace more hydrogen than can certain other metals. In order to investigate this matter further, suppose that 1 gram-atomic weight of sodium (22.997 g.), 1 gram-atomic weight of zinc (65.38 g.), and 1 gram-atomic weight of aluminum (26.97 g.) are each treated separately with an excess of dilute sulfuric acid. If the hydrogen liberated in each case is collected and the volume corrected to standard conditions, the results will be

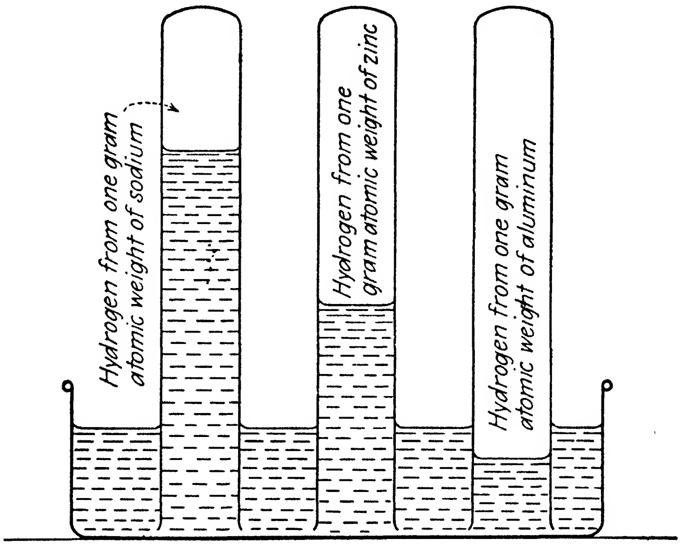


FIG. 39.—The relative volumes of hydrogen liberated by gram-atomic weights of the metals sodium, zinc, and aluminum.

of the character indicated in Fig. 39. These results, together with the equations for the reactions (Sec. 8.1), make evident the facts that

1 gram atom of Na displaces 1 gram atom of H
1 gram atom of Zn displaces 2 gram atoms of H
1 gram atom of Al displaces 3 gram atoms of H

With this in mind consider the four formulas HCl, H_2O, NH_3, and SiH_4. Apparently, elements differ not only in their ability to displace hydrogen from its compounds but also in their ability to hold hydrogen in combination. From the three cases just cited it may be concluded that

1 gram atom of Cl combines with 1 gram atom of H
1 gram atom of O combines with 2 gram atoms of H
1 gram atom of N combines with 3 gram atoms of H
1 gram atom of Si combines with 4 gram atoms of H

The property of elements having to do with what might be called their *combining capacity* is known as *valence.* **The number of atoms of hydrogen displaced by or combined with one atom of a given element is a measure of the valence of that element.** Thus, the valence of sodium = 1, zinc = 2, aluminum = 3, chlorine = 1, oxygen = 2, nitrogen = 3, and silicon = 4. Some elements exhibit more than one valence.

The foregoing definition of valence is not entirely satisfactory. It offers no explanation as to why, for example, 1 atom of sodium can displace only 1 atom of hydrogen whereas 1 atom of zinc can displace 2 atoms of hydrogen. To explain this difference a more intimate knowledge of the nature of the atoms concerned is required. As an ad interim compromise, valence may be looked upon merely as a number that represents the "combination value" or "displacement value" of each kind of atom.

Valence of Common Elements and Radicals. If the valences of a few of the elements are known together with the formulas of a few simple compounds, the formulas for many compounds may be deduced readily. Suppose, for example, that one wished to write the correct formula for the compound formed by the direct union of magnesium and nitrogen, Mg_xN_y. From the known formula NH_3, it is seen that the valence of nitrogen is 3. Magnesium forms a compound having the formula $Mg(OH)_2$, and from the formula for water [H(OH)] the valence of the (OH) radical must be 1. If the valence of the (OH) radical is 1, then that of Mg must be 2. Hence, there may be written,

TABLE 9
VALENCE OF COMMON ELEMENTS

Univalent (valence = 1)	Divalent (valence = 2)	Trivalent (valence = 3)
Metals:	Cd Mg	
Na	Ca Mn	Al
K	Ba Hg	Bi
Ag	Cu Sn	Fe
Cu	Fe Zn	Cr
Hg	Pb	
Nonmetals:*	O	
Br Cl	S	N
F I	....	P
H		B

* The nonmetals carbon and silicon commonly have a valence of 4.

$\overset{\text{II}}{Mg}_x\overset{\text{III}}{N}_y$. In a binary compound, each kind of atom must contribute the same total number of units of valence. Thus, if one writes $\overset{\text{II}}{Mg}_3\overset{\text{III}}{N}_2$, magnesium contributes $3 \times \text{II} = 6$ and nitrogen contributes $2 \times \text{III} = 6$ units of valence, and Mg_3N_2 is the correct formula for magnesium nitride.

For reference, there are collected in Table 9 the valences of the more common metals and nonmetals. Elements that commonly exhibit more than one valence are listed in more than one column. The names, formulas, and valences of the common radicals are listed in Table 10.

TABLE 10
COMMON RADICALS

Name	Formula	Valence
Ammonium	NH_4	1
Hydroxyl (or hydroxide)	OH	1
Nitrate	NO_3	1
Acetate	$C_2H_3O_2$	1
Chlorate	ClO_3	1
Sulfate	SO_4	2
Sulfite	SO_3	2
Carbonate	CO_3	2
Phosphate	PO_4	3
Arsenate	AsO_4	3

Equation Writing. Suppose that it is required to write an equation for the reaction between cadmium and phosphoric acid.

$$Cd + H_3PO_4 \rightarrow Cd_x(PO_4)_y + H_2$$

The valence of Cd is 2, that of the phosphate radical is 3; hence, the correct formula for the salt, cadmium phosphate, must be $Cd_3(PO_4)_2$, and

$$Cd + H_3PO_4 \rightarrow Cd_3(PO_4)_2 + H_2$$

The formula, $Cd_3(PO_4)_2$, requires that at least 3 atoms of Cd and 2 molecules of H_3PO_4 be used,

$$3Cd + 2H_3PO_4 \rightarrow Cd_3(PO_4)_2 + H_2$$

and the use of $2H_3PO_4$ provides a total of 6 atoms of hydrogen or 3 molecules, $3H_2$. The complete and balanced equation therefore is

$$3Cd + 2H_3PO_4 \rightarrow Cd_3(PO_4)_2 + 3H_2$$

8.5. Commercial Methods for the Preparation of Hydrogen

Of the methods given for the laboratory preparation of hydrogen, only the reaction between iron and steam is suitable for industrial application, and it is so used only to a limited extent. Some hydrogen is produced commercially by the catalytic decomposition of ammonia,

$$2\overline{NH_3} \rightarrow \overline{N_2} + 3\overline{H_2}$$

and some is obtained as a by-product of the production of chlorine, alcohols, and other chemicals.

Bosch Process. The chief commercial method for the production of hydrogen is known as the Bosch process and involves the reaction between steam and hot carbon.

$$C + \overline{H_2O} \rightarrow \overline{CO} + \overline{H_2}$$

The mixture of carbon monoxide and hydrogen is known as *water gas*. The carbon monoxide then reacts with additional steam to form carbon dioxide and more hydrogen.

$$\overline{CO} + \overline{H_2O} \rightarrow \overline{CO_2} + \overline{H_2}$$

The separation of the CO_2 and H_2 is accomplished by dissolving the CO_2 in water under high pressures, under which conditions only a very small quantity of the hydrogen is dissolved.

Preparation from Methane. A method similar to the Bosch process is that which depends upon the reaction between methane, CH_4 (which is the chief component of natural gas) and steam,

$$\overline{CH_4} + \overline{H_2O} \rightarrow \overline{CO} + 3\overline{H_2}$$
$$\overline{CO} + \overline{H_2O} \rightarrow \overline{CO_2} + \overline{H_2}$$

The CO_2 and H_2 are separated by the same method as that described in connection with the Bosch process. Hydrogen is also produced commercially by decomposing methane in contact with refractory bricks at 1000° to 1100°C.

Preparation by the Electrolysis of Water. It was pointed out in Sec. 4.1 that the decomposition of water by means of an electric current provides a means of securing oxygen gas on a commercial scale. At the same time hydrogen gas is liberated.

$$2H_2O \rightarrow 2\overline{H_2} + \overline{O_2}$$

By suitable arrangement of apparatus the two gases may be collected separately. Although this method is not so extensively used as the two preceding ones, it is of interest because it permits the simultaneous production of two common and important gases.

8.6. Physical Properties of Hydrogen

Hydrogen is a colorless, odorless, tasteless gas which is soluble in water only to the extent of 1.78 cc. per 100 cc. of water at 20°C. It is the lightest known gas, having a density of 0.0899 g. per liter at S.T.P. and is nearly 14.5 times lighter than air. Other significant physical properties of hydrogen are critical temperature = −239.9°C., boiling temperature = −252.78°C., and freezing temperature = −259.2°C.

8.7. Chemical Behavior of Hydrogen

Under suitable conditions, hydrogen combines with all the nonmetals except the inert gases and with many of the metals as well. The compounds with the metals are called *hydrides;* those with the nonmetals are given other names. Most reactions between hydrogen and the elements require elevated temperatures.

$$2Na + H_2 \rightarrow \underset{\text{Sodium hydride}}{2NaH}$$

$$Ca + H_2 \rightarrow \underset{\text{Calcium hydride}}{CaH_2}$$

$$S + H_2 \rightarrow \underset{\text{Hydrogen sulfide}}{H_2S}$$

$$2P + 3H_2 \rightarrow \underset{\text{Phosphine}}{2PH_3}$$

Of particular importance is the formation of water by the direct union of hydrogen and oxygen. This reaction does not occur at all at ordinary temperatures but occurs slowly at 500°C. and almost instantaneously at 700°. This reaction is catalyzed by finely divided platinum (Pt), palladium (Pd), iron, iron oxide, etc. These and other catalysts have the property of absorbing (or adsorbing) huge quantities of hydrogen on their surfaces and the catalytic action probably is due to the resulting localized increase in the concentration of hydrogen with resultant increase in the rate of combination with oxygen at the surface of the catalyst. For example, 1 volume of powdered palladium metal is capable of absorbing about 800 volumes of hydrogen at ordinary temperatures.

When two parts by volume of hydrogen and one part by volume of oxygen are brought together, the mixture may be caused to react with explosive violence by a flame or an electric spark. This behavior is the cause of numerous industrial accidents and of explosions suffered by balloons and other lighter-than-air craft filled with hydrogen. Such craft are subject to the hazard of explosions due to ignition of an explosive mixture of hydrogen and air by electric sparks, lightning,

flames, or incendiary bullets. Pure hydrogen burns with a colorless but extremely hot flame.

Reducing Action of Hydrogen. At suitably elevated temperatures, hydrogen reacts with many compounds to remove and combine with one or more of the elements contained in the compound. At high temperatures hydrogen removes and unites with the oxygen contained in the oxides of certain metals (Fig. 40).

$$CuO + \overline{H_2} \rightarrow Cu + \overline{H_2O}$$
$$Fe_3O_4 + 4\overline{H_2} \rightarrow 3Fe + 4\overline{H_2O}$$

These changes are known as *reduction* reactions and the metal oxides are said to be *reduced*, but just as the term *oxidation* is not restricted

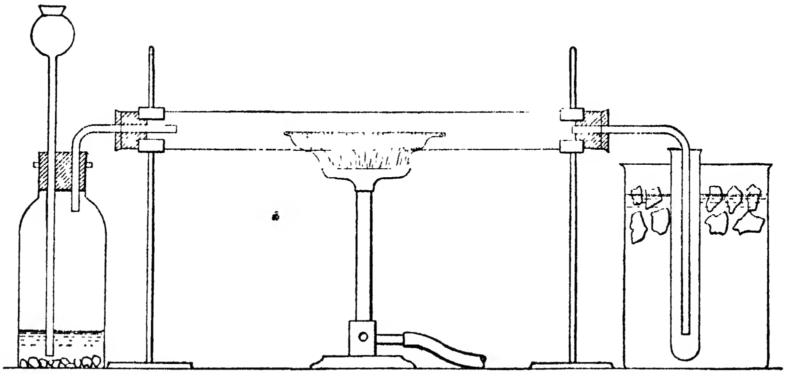


FIG. 40.—Laboratory apparatus for use in the reduction of metal oxides by means of hydrogen. The oxide to be reduced is placed in a porcelain boat contained in a glass tube which is connected to the hydrogen generator shown on the left. Water formed in the reaction may be condensed in the test tube cooled in an ice bath.

to reactions of oxygen, so the term *reduction* may be and is applied to many reactions that do not involve hydrogen.

It is enlightening to consider, in terms of the order of activity of metals, the ease with which oxygen can be removed from oxides of the metals. Starting at the bottom of the list (Table 8) oxygen may be removed readily from the oxides of gold, platinum, mercury, and silver merely by the application of heat. From silver to and including iron, the removal of oxygen from the corresponding oxides becomes increasingly difficult but may be accomplished by reduction with hydrogen. The oxides of the metals above iron are still more stable (resistant to decomposition) and the removal of oxygen from these oxides requires still more vigorous modes of chemical attack. From all this it may be concluded that the metals that stand highest in the order of activity form, in general, the most stable compounds.

8.8. Uses of Hydrogen

In the United States alone the annual consumption of hydrogen in the various chemical industries reaches enormous proportions. Large quantities of hydrogen are used in the manufacture of ammonia which in turn is converted into fertilizers and explosives. Fat substitutes are produced by the "hydrogenation" of liquid oils of animal and vegetable origin. From 1000 to 5000 cu. ft. of hydrogen is required to convert 1 ton of cottonseed oil to a semisolid mass which may be used as a substitute for lard or in the manufacture of soap. Another large-scale use of hydrogen is the hydrogenation of coal. In this process, a part of the coal is changed to a light oil from which gasoline and lubricating oils may be obtained. Despite the danger of explosions, hydrogen is still used for the inflation of balloons and dirigibles in those countries which are prevented from obtaining helium by the monopolistic control exercised by the government of the United States.

EXERCISES

1. In the language of chemistry, what is the meaning of the terms (*a*) radical, (*b*) valence?

2. Write equations representing three laboratory methods and three commercial methods for the preparation of hydrogen.

3. Knowing that both CO and H_2 are only sparingly soluble in water, suggest a method whereby hydrogen could be separated from carbon monoxide.

4. Write formulas for the simple binary compounds formed by the direct union of the following pairs of elements:

(*a*) Potassium and sulfur
(*b*) Barium and fluorine
(*c*) Aluminum and iodine
(*d*) Bismuth and nitrogen
(*e*) Silver and phosphorus
(*f*) Boron and bromine

5. It is proposed to produce metals by removal of oxygen (reduction) of oxides. For the reactions suggested below, write equations for those cases in which the suggested reaction will occur.

(*a*) Ag_2O + heat
(*b*) ZnO + heat
(*c*) NiO + hydrogen
(*d*) Bi_2O_3 + hydrogen
(*e*) Al_2O_3 + hydrogen
(*f*) CuO + heat

6. Each of the following pairs of substances represents a combination of metal and acid for use in the preparation of hydrogen. For those cases in which the formation of hydrogen is possible, write equations for the reactions.

(*a*) Tin + hydrochloric acid
(*b*) Magnesium + acetic acid
(*c*) Copper + phosphoric acid
(*d*) Calcium + hydrochloric acid
(*e*) Manganese + nitric acid
(*f*) Cadmium + acetic acid

7. Calculate the weight of tin required to produce 22 tons of hydrogen gas.

8. If hydrogen is to be produced by the reaction between magnesium and water, what weight of water will be consumed in the production of 89.6 liters of hydrogen (measured at S.T.P.)?

9. Calculate the weight of lead metal that will result if 10 lb. of lead oxide are reduced by means of hydrogen gas.

10. If magnesium reacts with hot water, why is it possible to use Mg-Al alloys in airplane construction?

SUGGESTED READING

Journal of Chemical Education

Alexander and Byers, Hydrogen from Iron and Water, **9,** 916 (1932).

Bartlett, Atomic Hydrogen Flames, **4,** 39 (1927).

Flood, Valence Defined, **12,** 132 (1935).

Industrial and Engineering Chemistry

Kanolt and Cook, Production of Pure Hydrogen for Liquefaction, **17,** 183 (1925).

Claude, The Manufacture of Hydrogen by the Partial Liquefaction of Water Gas and Coke-oven Gas, **14,** 1118 (1922).

Karzhavin, Hydrogen from Natural Gas, **28,** 1042 (1936).

Brownlie, Bulk Production of Hydrogen, **30,** 1139 (1938).

CHAPTER IX

SOLUTIONS

The chemical changes described in detail or used as illustrations up to this point have been concerned for the greater part with pure gases, liquids, or solids. Hereafter, greater emphasis will be placed upon reactions involving mixtures, but mixtures of the particular variety known as *solutions*. The manufacture of many useful chemical products and the great majority of the more important types of chemical change involve solutions either directly or indirectly.

9.1. Nature of Solutions

Everyone is familiar with the fact that some liquids have the ability to wet the surfaces of solids. This wetting effect is the result of an attraction between the molecules of the liquid and those of the solid. In many cases, these attractive forces succeed in dislodging single molecules (or larger particles) of the solid and in surrounding the dislodged molecules completely by molecules of the liquid. Under these circumstances, the solid is said to dissolve in the liquid and the resulting mixture of solid dissolved in liquid is called a *solution*.

If the dissolved substance exists in the solution in the form of single molecules or very small clusters or groups of molecules uniformly distributed throughout the body of the liquid, the mixture is perfectly homogeneous and the dissolved particles show no tendency to settle out under the influence of gravity. A mixture of this character is known as a *true solution*. If, however, the particles consist of large clusters or groups of molecules, the resulting mixture will not be perfectly homogeneous, the particles will show at least a limited tendency to settle under the influence of gravity, and the mixture is said to be a *colloid*. There is yet another possibility. Suppose that the particles are of such size (very large groups of molecules—particles visible to the unaided eye) that the mixture is obviously heterogeneous and the particles can be made to remain distributed throughout the liquid only by continuous stirring. Under these conditions the mixture is properly described as a *suspension*. The distinction, then, between true solutions, colloids, and suspensions is largely one of relative particle size.

A clear distinction must also be drawn between solutions and compounds. It has been established already that compounds are sub-

stances having absolutely definite composition, and this is certainly not true of solutions. One may dissolve 1 g., 10 g., or 100 g. of cane sugar in 1 liter of water, and in each case there will be formed a true solution. The composition of a true chemical compound, however, is not subject to any such variations. Accordingly, it is seen that solutions differ from compounds in that the composition of solutions is variable.

9.2. Composition of Solutions

In view of the foregoing ideas concerning the nature of solutions, **a solution may be defined as a homogeneous mixture the composition of which may be varied between certain definite limits.** Every solution must consist of at least two components: a *solute* and a *solvent.* These two components are usually designated in terms of the relative quantities involved; the component present in larger quantity is usually called the solvent. For example, if a solution consists of a homogeneous mixture of 10 g. of ordinary table salt and 100 g. of water, the salt is the solute and the water is the solvent. If, however, a homogeneous mixture consisted of 100 g. of water and 100 g. of alcohol, a clear distinction between solute and solvent could not be made except on some wholly arbitrary basis.

9.3. Classification of Solutions on the Basis of the Physical State of the Solute and Solvent

Unless some thought is given to the matter, one is likely to get into the habit of thinking of solutions only in terms of solutions of solids in liquids. Although it is true that most common solutions are of this variety, there are eight other possible types of mixtures. The nine types, together with suitable examples, in the cases of those which frequently exist as true solutions include:

1. *Solutions of Gases in Gases.* Example: air or any other homogeneous mixture of gases.

2. *Solutions of Gases in Liquids.* Example: "carbonated" soft drinks which consist of carbon dioxide gas (and other solutes) dissolved in water.

3. *Solutions of Gases in Solids.* Example: the absorption of hydrogen by palladium (Sec. 8.7) may be looked upon as a situation in which a gas is dissolved in a solid.

4. *Solutions of Liquids in Liquids.* Example: a mixture of alcohol and water.

5. *Solutions of Liquids in Solids.* Example: the liquid metal mercury forms solutions with certain solid metals such as gold.

6. *Solutions of Solids in Liquids.* Example: sugar dissolved in water, or any other of the many familiar examples of this the most common type of solution.

7. *Solutions of Solids in Solids.* Example: the alloy known as brass consists of a *solid solution* of zinc in copper.

8. *Mixtures of Liquids and Gases.*

9. *Mixtures of Solids and Gases.*

Any substance that dissolves in a given solvent is said to be *soluble* in that solvent.

9.4. Classification of Solutions in Terms of the Quantity of Solute

In speaking of the concentration of solutes present in solutions (*i.e.*, the quantity of solute per unit volume of solution) the chemist uses certain terms which are somewhat indefinite but which nevertheless convey real meanings. Two purely relative designations are the terms *concentrated* and *dilute*. Concentrated solutions are understood to be ones that are relatively rich in solute as compared with dilute solutions in which the concentration of solute is relatively small. In an effort to qualify these already indefinite terms, the chemist employs numerous variations. Thus, one speaks of "highly concentrated," "very dilute," "moderately dilute" solutions, etc.

Saturated Solutions. If a large cube of sugar is allowed to stand in the presence of a quantity of water insufficient to dissolve all of the sugar, molecules of the solid sugar go into solution and distribute themselves uniformly throughout the body of the liquid. At any given temperature, this process will continue and, as the concentration of sugar molecules in solution increases, some of these molecules will leave the solution and return to the solid. In time, the rate at which molecules are leaving the solution and returning to the solid becomes equal to the rate at which molecules are leaving the solid and entering the solution (Fig. 41). In other words, a condition of dynamic equilibrium becomes established, and under these conditions the solution is said to be *saturated*. Accordingly, **a saturated solution is one**

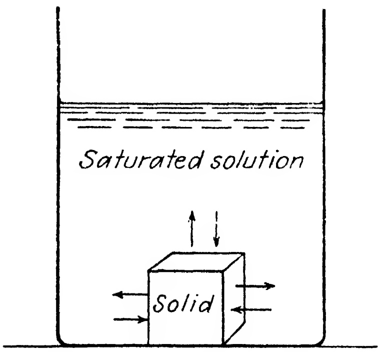


FIG. 41.—Equilibrium between a solid and a saturated solution.

which is in equilibrium with an excess of the undissolved solute.

It is easy to prove that a condition of dynamic equilibrium exists in a saturated solution. If a broken or otherwise imperfect crystal is suspended (by means of a fine wire) in a saturated solution in which the solute is of the same composition as the crystal, the solution will remain saturated and the total weight of the crystal will not change. In time, however, the imperfection in the crystal will tend to be repaired. That is, solute molecules leave from any or all surfaces of the crystal but return from the solution to the crystal primarily in the region where the imperfection exists.

Standard Solutions. In studying the properties of solutions and in carrying out chemical reactions involving solutions, it is frequently necessary to use solutions containing definite known quantities of solute. Any solution of known concentration is classed as a *standard solution.* There are several different kinds of standard solutions in common use, *e.g.*, *molar* and *molal* solutions.

A molar solution is one which contains one gram-molecular weight of a solute dissolved in enough solvent to make exactly one liter of solution. For example, if 1 gram-molecular weight (1 mole) of alcohol (C_2H_6O) (46 g.) is dissolved in enough water to make 1 liter of solution, the resulting solution is *one molar* (1 M). If 2 moles ($2 \times 46 = 92$ g.) are dissolved in enough water to make 1 liter of solution, this solution is *two molar* (2 M), etc. Similarly, 1 liter of solution containing $\frac{1}{10}$ mole of alcohol ($\frac{1}{10} \times 42 = 4.2$ g.) is said to be *one-tenth molar* (0.1 M). Solutions prepared on the basis of molarity are particularly useful in the study of those properties of solutions which depend upon the number of molecules contained in a given volume of solution. One liter of a 1 M solution of any solute contains, of course, 6.02×10^{23} molecules of solute; a 0.5 M solution contains just one-half this number of molecules, etc.

A molal solution is one which consists of one gram-molecular weight of solute dissolved in 1000 grams of solvent. Since in dilute solutions 1000 g. of solvent and 1 liter of a water solution are not greatly different, a one-tenth molal (0.1 m) and a one-tenth molar (0.1 M) solution may be practically identical. On the other hand, one molal and one molar solutions might be appreciably different. Of the two, molal solutions are less frequently employed.

A third kind of standard solution is the *normal* solution. This type will be discussed in connection with the study of reactions between acids and bases (Sec. 11.9).

9.5. Solubility

Returning for the moment to the discussion of saturation and to Fig. 41, it will be recalled that the extent to which sugar may be dissolved by a fixed quantity of water is limited. The quantity of solute that can be dissolved in a given quantity of solvent is called the *solubility* of that solute. Although any convenient units may be used, solubilities are usually expressed in grams of solute per 100 g. (or 100 ml.) of solvent. The solubilities of a few solids in water are listed in Table 11 together with the descriptive terms usually employed in referring to substances having solubilities of the indicated order of magnitude.

Not all solutes are of limited solubility. The solubility of gases in gases is without limit, since the composition of a gaseous mixture may be adjusted to any desired composition. In some cases, the solubility of liquids in liquids is limited, while in other liquid-liquid mixtures no such limitation exists and the two liquids are said to be *miscible* in all proportions.

TABLE 11
SOLUBILITY OF SOME SOLIDS IN WATER

Solute	Solubility, g. solute per 100 ml. water	Qualitative description
Sodium chlorate ($NaClO_3$)	97.16	Very soluble
Magnesium nitrate [$Mg(NO_3)_2$]	74.31	
Sodium chloride ($NaCl$)	35.86	Moderately soluble
Potassium nitrate (KNO_3)	30.34	
Barium hydroxide [$Ba(OH)_2$]	3.7	Sparingly or slightly soluble
Lead chloride ($PbCl_2$)	1.49	
Calcium sulfate ($CaSO_4$)	0.2	
Zinc fluoride (ZnF_2)	0.005	Insoluble*
Silver chloride ($AgCl$)	0.00013	
Barium sulfate ($BaSO_4$)	0.00023	

* No substance is absolutely insoluble, but for all practical purposes substances of extremely low solubility may be so considered.

9.6. Factors That Influence Solubility

The solubility of a pure solute in a pure solvent is definite only under specified experimental conditions. The solubility of solids in liquids is markedly dependent upon temperature, while the solubility of gases in liquids is influenced by both temperature and pressure.

Two additional factors that may have a bearing on the solubility of a given solute are (1) the presence of other solutes and (2) the occurrence of a chemical reaction between the solute and the solvent.

As a general rule, each solute dissolves in and saturates the solution without being greatly affected by the presence of other solutes, but this is not always true. An exception to the general rule is found in the influence of the presence of hydrogen chloride upon the solubility of sodium chloride in water. If the solubility of NaCl in water is measured accurately, it will be found to be, for example, 35.86 g. of NaCl per 100 ml. of water at 18°C. If now, the solubility of NaCl in water saturated with hydrogen chloride gas is determined, the solubility will be found to be much less than that of the above value. To prove the same point by another approach, if HCl gas is bubbled into a saturated solution of NaCl in water, crystals of NaCl will separate from the solution. In still other instances, the solubility of one solute is enhanced by the presence of one or more other solutes.

Chemical interaction of solute and solvent (or of one solute and another) also is encountered frequently. Thus, salts that combine with molecules of the solvent (Sec. 10.6) are usually more soluble than those salts which dissolve without chemical combination with the solvent. The extensive solubility of ammonia in water is to some extent due to the combination of molecules of ammonia with molecules of the solvent to form the base known as *ammonium hydroxide.*

$$\overline{NH_3} + HOH \rightarrow NH_4OH$$

Bromine is only slightly soluble in water but is extensively soluble in water containing dissolved sodium bromide, NaBr, and this enhanced solubility is believed to result from reaction between the bromine and sodium bromide. It is extremely difficult, if not impossible, to draw a sharp line of demarcation between those processes of solution which do and those which do not involve chemical changes of some sort. Unless otherwise specified, the following discussion (as well as that of Chap. X) assumes that chemical reaction between solvent and solute either is absent or is without bearing upon the topics under consideration.

Influence of Temperature and Pressure upon the Solubility of Gases in Liquids. When a glass container filled with ice water (at 0°C.) is allowed to stand and warm to room temperature, small bubbles of gas are seen to collect around the walls of the container and finally to rise to the surface and escape from the solution. This simple experiment proves that the solubility of the gas (in this case the air that was already dissolved in the water) is less at room temperature

than it is at 0°C. In general, the solubility of gases in liquids *decreases* with an increase in temperature.

At any given temperature, the solubility of gases *increases* with increase in pressure and is directly proportional to the applied pressure. This is a statement of *Henry's law*. If a gas is confined over water in a cylinder fitted with a movable piston (Fig. 42) and the piston is at such position (*A*) that the pressure upon the gas is 1 atm., a certain definite quantity of the gas is dissolved by the available solvent. If now the piston is moved so that the gas is placed under a pressure of 2 atm. (position *B*), the solubility of the gas will be doubled. If a mixture of gases is used, each gas dissolves to an extent that is dependent only upon its partial pressure in the mixture and not upon the presence of the other gases in the mixture.

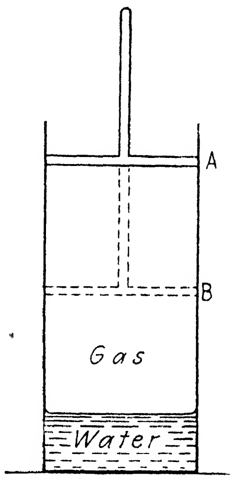


FIG. 42.—Influence of pressure upon the solubility of a gas in a liquid.

The sequence of events that accompany the opening of a cold bottle of soda water serves to illustrate the effects of both pressure and temperature. When the cap is first removed, the sudden evolution of carbon dioxide gas provides evidence that this gas is less soluble at atmospheric pressure than at the pressure existing within the unopened bottle. The effect of temperature is shown by the progressive liberation of carbon dioxide as the contents of the bottle slowly warm to the temperature of the surrounding atmosphere.

Influence of Temperature upon the Solubility of Solids in Liquids. In general, the solubility of solids in liquids *increases* with increase in temperature. However, a few solids such as calcium sulfate ($CaSO_4$), calcium chromate ($CaCrO_4$), cerous sulfate [$Ce_2(SO_4)_3$], and calcium hydroxide [$Ca(OH)_2$] behave in just the opposite manner. The solubility of a number of solids in water and their variation in solubility over the temperature range of 0° to 100°C. are shown graphically in Fig. 43. If a solution is saturated at 25° and the temperature is then increased to 30°, more solute dissolves until a new equilibrium is established (*i.e.*, the solution again becomes saturated) at the higher temperature. If the solution is then cooled to the original temperature of 25°, crystals of the solute will separate from the solution in an amount equal to that which dissolved because of the increase in temperature. This behavior is observed in all cases except those in which supersaturation occurs. Occasionally crystals do not

separate immediately when a saturated solution is cooled. At the lower temperature, then, such a solution contains more dissolved solute than is normally present at that temperature and is therefore described as a *supersaturated* solution. Crystals usually may be obtained readily from a supersaturated solution by stirring the solu-

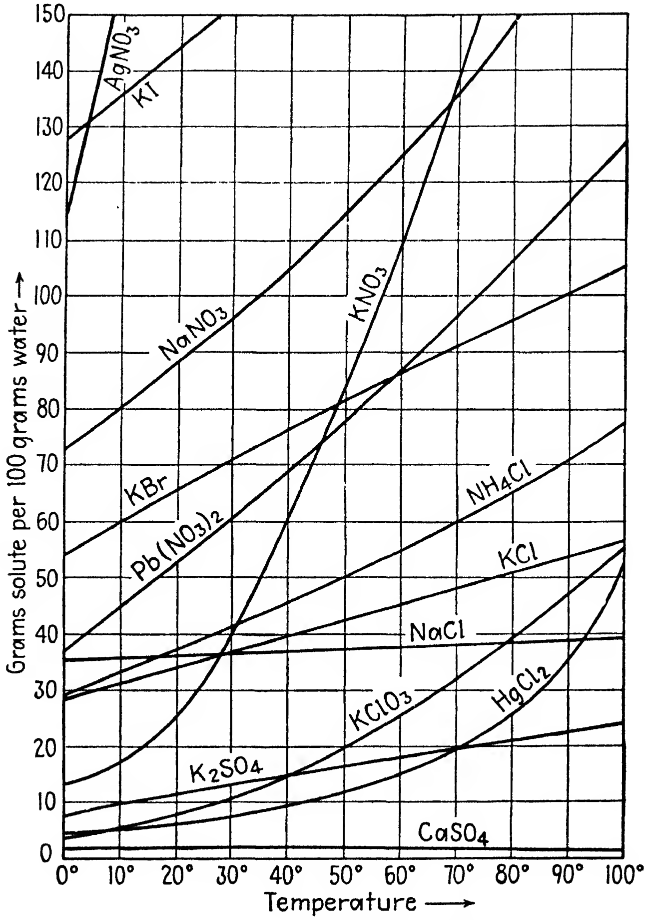


FIG. 43.—The relation between the solubility of certain salts and temperature.

tion vigorously or by inoculating or "seeding" the solution with a crystal of the same composition as the solute. Even tiny dust particles which serve as centers about which crystal growth may occur are sufficient to induce crystallization from a supersaturated solution.

Rates of Solution. Particularly in connection with solutions of solids in liquids, care should be exercised in order to avoid confusion between the *extent of solubility* and the *rate of solution.* At any given

temperature, a particular sample of a solid may be very soluble and yet appear to dissolve only slowly. The rate at which a solid dissolves in a liquid depends upon the extent of contact between the solvent and the surface of the solid. Thus, a single crystal of salt weighing 1 g. will dissolve in water much more slowly than will 1 g. of the finely powdered salt in the same quantity of water at the same temperature. If one wishes to increase the rate at which a solid dissolves in a liquid, increased surface contact between solid and solvent may be had by the use of a finely divided solid and by agitating (stirring) the mixture.

9.7. Recrystallization as a Means of Purifying a Solid

When a solution containing two solutes is cooled, crystals of the less soluble solute will begin to separate from the solution as soon as the saturation point of this solute is reached. The crystals that appear will be of the particular crystal type characteristic of the given solid substance and usually will not contain molecules of the more soluble solute. Apparently, the molecules of the second substance usually do not fit into the particular crystal pattern that is being built. Should the solution be cooled sufficiently or should the two solutes be of comparable solubility, each usually crystallizes independently and in its own characteristic crystalline form.

Advantage is taken of this behavior in the purification of solids. Suppose, for example, that it is desired to obtain pure potassium chlorate from an impure sample consisting of 40 g. of $KClO_3$ contaminated with 10 g. of KCl. If this solid mixture is dissolved in 100 ml. of water at 100°C., then cooled, crystals of $KClO_3$ will begin to separate from the solution when the temperature reaches about 80° (see Fig. 43) and will continue to separate as the temperature is lowered further. Even if cooled to a temperature near 0°C., the KCl will remain in solution since the solubility of KCl is about 13 g. per 100 ml. of water at 0°. The crystals of $KClO_3$ may be separated from the solution by filtration.

The foregoing illustration gives a somewhat idealized picture of the process of purification by recrystallization. In actual practice, the first "crop" of crystals obtained is seldom of a high degree of purity, and succeeding crops (which may be filtered off periodically as the temperature is lowered through certain intervals) are still more greatly contaminated by small quantities of the impurities. This is particularly true if the solubility of the impurities is not greatly different from that of the desired pure substance. However, if the first crops of partly purified material are again recrystallized from water, a product of the desired degree of purity may be obtained. A solid that

has been purified in this manner is said to have been *recrystallized* and, if the crops of crystals that separate from the solution as the temperature is lowered through definite intervals are collected separately, the process is referred to as one involving *fractional crystallization.*

9.8. Common Solvents

From the preceding discussions it is evident that one may choose from an almost unlimited variety of solvents including solids, liquids, and gases. In spite of this fact, however, the great bulk of presently available knowledge of solutions centers about a single solvent, *viz.*, water. The fact that chemical developments of the past have emphasized the chemistry of solutions in water suggests that real opportunities for future developments lie in the study of solvents other than water. To the extent that it serves as a solvent for inorganic substances, water occupies a unique position. It is, on the other hand, a relatively poor solvent for organic substances. Solutions in which water is the solvent are commonly referred to as *aqueous* solutions. Other solutions (or substances in general) that contain no water are said to be *anhydrous.*

In recent years, two additional inorganic solvents have come to be used more commonly in chemical work. These are ammonia and sulfur dioxide, both of which are gases under ordinary atmospheric conditions but which may be employed as liquid solvents at low temperatures and/or under pressure. In addition to being fairly good solvents for inorganic solutes, ammonia and sulfur dioxide are also excellent solvents for organic substances.

Some of the more important organic solvents are acetone, alcohols such as methyl and ethyl alcohols, diethyl ether, and benzene. The chemical nature of these materials will be considered in some detail in Chaps. XXXIII to XXXVI. In general, these organic liquids serve well as solvents for organic solutes but exhibit only very limited capacities to dissolve inorganic substances.

EXERCISES

1. Define the following terms: (*a*) solution, (*b*) solvent, (*c*) solute, (*d*) molar solution, (*e*) molal solution, (*f*) saturated solution.

2. Distinguish clearly between the following terms: (*a*) dilute and concentrated solutions, (*b*) standard solution and molar solution, (*c*) molar and molal solutions, (*d*) true solution, colloid, and suspension, (*e*) compound and solution.

3. What is meant when the following expressions are used: (*a*) an insoluble substance, (*b*) miscible liquids, (*c*) soluble in water, (*d*) a supersaturated solution, (*e*) the solubility of a substance?

4. How is the solubility of a gas in a liquid influenced (*a*) by an increase in pressure, (*b*) by a decrease in temperature?

5. What generalization may be made with regard to the influence of temperature upon the solubility of solids in liquids?

6. Determine the weight of solute required to prepare each of the following solutions:

(a) 1 liter of 0.5 *M* alcohol (C_2H_6O) solution
(b) 3 liters of 1 *M* sodium chloride solution
(c) ½ liter of 0.3 *M* glycerol ($C_3H_8O_3$) solution
(d) 100 ml. of 0.1 *M* hydrogen chloride solution

7. What difficulty would be encountered if one attempted to prepare a 1 *M* solution of silver chloride?

SUGGESTED READING

Journal of Chemical Education

DUNNING, PRATT, and LOWMAN, What Starts Precipitation from a Supersaturated Solution, **11**, 621 (1934).

ROHRMAN and TAYLOR, The Preparation of Large Crystals of Chrome Alum and Interpretation of Some Etch Figures, **6**, 473 (1929).

BATEMAN and FERNELIUS, Demonstration of a Negative Temperature Coefficient of Solubility, **14**, 315 (1937).

BACON, Use of Calcium Acetate in the Demonstration of a Substance Showing a Negative Coefficient of Solubility, **15**, 494 (1938).

KOBE, Demonstration of an Inverted Solubility Curve, **16**, 183, (1939).

FERNELIUS and JOHNSON, Liquid Ammonia as a Solvent, **5**, 664 (1928).

CHAPTER X

PHYSICAL PROPERTIES OF SOLUTIONS

From the study of the properties of liquids (Chap. VI), it should be recalled that each pure liquid is characterized by definite physical properties such as boiling temperature, freezing temperature, and vapor pressure. The following discussion is concerned with the manner in which these physical properties are altered by the presence of solutes. Throughout this discussion, only nonvolatile solutes will be considered. If the influence of a solute is to be studied, it is certainly desirable that it remain in the solution so that its effects may be studied over a period of time. Volatile solutes would also complicate the study of the vapor pressures of solvents since the solute molecules themselves would escape and exert measurable vapor pressures. Acids, bases, and salts are excluded for other reasons which will become apparent later.

10.1. Lowering of the Vapor Pressure

When a nonvolatile solute is dissolved in a pure solvent, the vapor pressure of the resulting solution is less than the vapor pressure of the pure solvent at the same temperature. The extent to which the vapor pressure of the solvent is lowered is directly proportional to the ratio of the *number* of solute molecules to the total number of molecules in the solution. Thus, 1 gram-molecular weight of napthalene ($C_{10}H_8$) (128 g. containing 6.02×10^{23} molecules) dissolved in acetone will lower the vapor pressure of acetone just exactly as much as will 1 gram-molecular weight of camphor ($C_{10}H_{16}O$) (152 g. also containing 6.02×10^{23} molecules), dissolved in an equal quantity of acetone. Consequently, it would seem that the lowering of the vapor pressure depends only upon the number and not upon the kind of solute molecules present. The correctness of this assumption becomes apparent when one attempts, in terms of the kinetic-molecular theory, to visualize the manner in which the presence of solute molecules operates to decrease the vapor pressure of the solvent.

The escape of solvent molecules from the liquid occurs at the surface of the liquid. In Fig. 44*a*, molecules in the surface of a pure liquid solvent are represented as being in equilibrium with solvent

molecules in the vapor state, and therefore exerting the normal solvent vapor pressure at the given temperature. In the solution (Fig. 44*b*), the exposed surface is partly occupied by molecules of the nonvolatile solute and the available surface from which the escape of solvent molecules can occur is correspondingly diminished. Furthermore, in the body of the liquid, those solvent molecules which have higher than average kinetic energies and which would tend to move to the surface and escape will be impeded by the presence of solute molecules. As a result, fewer solvent molecules can escape from the liquid to exert pressure upon the surface of the liquid. At the same temperature, an increase in the number of solute molecules would serve further to lower the vapor pressure.

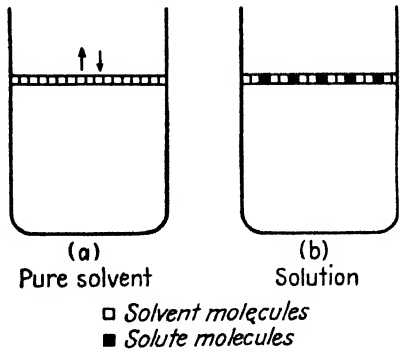


FIG. 44.—Comparison of the surface layer of molecules in a pure solvent and a solution.

Deliquescence. A practical example of the lowering of vapor pressure is found in the behavior of substances that exhibit the property of deliquescence. Some solids are so very soluble in water that they form solutions on their surfaces when exposed to an atmosphere containing sufficient water vapor. When solid zinc chloride ($ZnCl_2$) or potassium hydroxide (KOH), for example, is exposed to the air, its surface quickly becomes covered by a thin film of solution. This behavior is known as *deliquescence*, and the solid substance is said to be *deliquescent* or *hygroscopic*. Because of the presence of dissolved KOH, the vapor pressure of this solution is less than the partial pressure of the water vapor in the surrounding atmosphere. Consequently, the water vapor will enter the solution from the air and the solid will all be dissolved. Furthermore, water vapor from the atmosphere will continue to enter and dilute the solution until the vapor pressure of the solution becomes the same as (reaches equilibrium with) the partial pressure of water vapor in the atmosphere.

Use is made of this phenomenon in keeping down the dust on unsurfaced roads. Calcium chloride ($CaCl_2$) is a cheap commercial product which is extremely deliquescent. When sprinkled upon the surface of a dusty highway, the $CaCl_2$ attracts moisture from the atmosphere and forms a solution which moistens the road surface and prevents the rise of dust particles. This application is, of course, entirely useless in hot, arid climates where the partial pressure of water vapor in

the atmosphere is less than the vapor pressure of a saturated solution of calcium chloride.

10.2. Elevation of the Boiling Temperature

The boiling of a pure liquid has been pictured as the condition that obtains when the kinetic energy of the molecules of the liquid has been increased (by application of heat energy) to such extent that the vapor pressure of the liquid exceeds the opposing atmospheric pressure. At an atmospheric pressure of 760 mm., the boiling temperature of pure water is 100°C. If the temperature of water containing a nonvolatile solute is raised to 100°C., boiling does not occur; the kinetic energy of the water molecules is not large enough to overcome both the opposing atmospheric pressure and the interference offered by the solute molecules. This is simply another way of saying that the vapor pressure of the solution at 100°C. is less than the opposing atmospheric pressure for it has already been shown that the vapor pressure of a solution is less than that of the pure solvent at the same temperature. The result is that the temperature must be raised above 100° in order to cause the solution to boil.

Just how much elevation in temperature is required to produce boiling depends upon exactly the same factor that determines the extent of lowering the vapor pressure, *viz.*, the *number* of solute molecules present. At 760 mm., a solution consisting of 1 mole of sugar (342 g.) dissolved in 1000 g. of water boils at 100.515°C., which is exactly the same as the boiling temperature of a solution consisting of 1 mole of glycerol (92 g.) dissolved in 1000 g. of water. Both solutions boil at the same temperature despite the great difference in total weight of solute because both solutions contain exactly the same number of solute molecules. Excluding acids, bases, and salts, a 1-molal aqueous solution will boil 0.515° above the normal boiling temperature of pure water. With solvents other than water, the extent of elevation in boiling temperature is different from 0.515° but is nevertheless definite for each solvent.

Fractional Distillation. When a mixture of two liquids having different vapor pressures (and therefore different boiling temperatures) is heated, boiling will occur when the combined vapor pressures of the two liquids exceeds the opposing atmospheric pressure. The results obtained by continued boiling of such a mixture may be understood best in terms of a specific example. If a mixture consisting of equal volumes of alcohol (which boils at 78.4° at 1 atm.) and benzene (which boils at 80.4° at 1 atm.) is placed in the boiler of a distillation apparatus (Fig. 45) and heated to boiling, the vapors that leave the liquid may

be condensed upon coming into contact with the cold inner surface of the condenser and collected in a suitable container. The first liquid (distillate) to be collected will be a mixture consisting largely of alcohol but containing some benzene. As the distillation continues, the temperature rises and the vapors that leave the liquid will become increasingly richer in benzene (the higher boiling component of the mixture) and will contain less and less alcohol. This must occur if boiling is to continue. Initially, the alcohol exerted the major fraction of the total

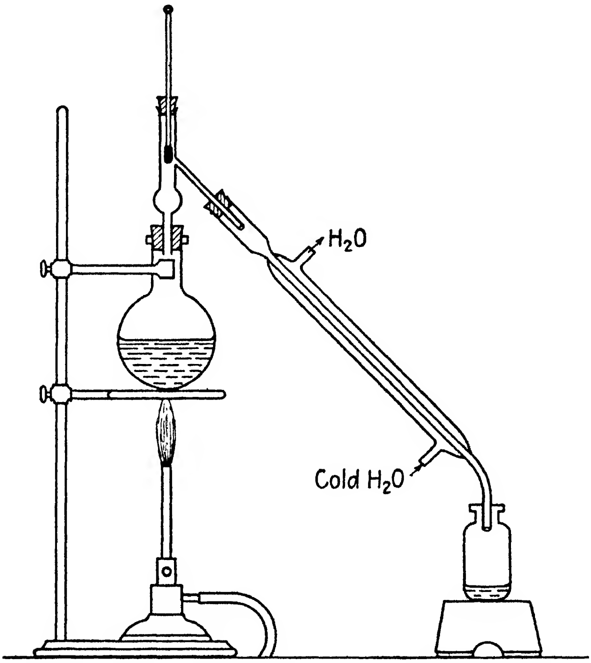


Fig. 45.—Apparatus for fractional distillation.

vapor pressure of the mixture. As the alcohol is distilled from the mixture, the temperature must increase enough to raise the partial pressure of benzene sufficiently to overcome the loss in total vapor pressure occasioned by the removal of alcohol. Finally, the last vapors to leave the liquid are relatively richer in benzene and contain but little alcohol. If the vapors are condensed and collected in, for example, three portions or fractions, the first will be largely alcohol, the last collected will be largely benzene, and the middle fraction will be a mixture of the two. If the first and third fractions are separately subjected to one or more additional distillations of the same sort, pure alcohol and pure benzene may be secured.

This process is known as *fractional distillation.* It is employed extensively in the separation of crude petroleum into fractions such as gasoline, kerosene, or lubricating oil. Many other liquid industrial products are separated and purified by similar operations.

10.3. Lowering of the Freezing Temperature

At the freezing temperature of a pure solvent, solid exists in equilibrium with liquid and the vapor pressure of the solid is identical with that of the liquid. For water at a pressure of 1 atm., this condition is realized at 0°C. When the temperature of a dilute aqueous solution of a nonvolatile solute is lowered to the freezing temperature, only crystals of the solvent appear and this is found to occur at a temperature *below* the freezing temperature of the pure solvent. At this lower temperature, the vapor pressure of the solvent crystals is equal to the solvent vapor pressure of the solution; a condition which can be realized only at a temperature lower than the normal freezing temperature of the pure solvent.

Again, the situation is amenable to explanation on the basis of the kinetic-molecular theory. Homogeneous distribution of solute molecules throughout the body of the liquid increases the average distance between solvent molecules. The force of attraction between molecules, which tends to arrange the molecules of the solvent into the definite geometric pattern of the crystal, cannot be so effective over this greater average distance. In order for the forces of attraction to operate, it is necessary that the kinetic energy of the solvent molecules be lessened, since it is the kinetic energy that acts in opposition to the forces of attraction or cohesion. The kinetic energy is decreased by lowering the temperature below the normal freezing temperature of the pure solvent. The extent to which the temperature must be lowered is obviously dependent upon the *number* of solute molecules present in the particular solution.

Again excluding acids, bases, and salts, 1 mole of sugar (342 g.), 1 mole of glycerol (58 g.), or 1 mole of any other nonvolatile solute dissolved in 1000 g. of water (*i.e.*, 1 *m* solutions) will form a solution having a freezing temperature of −1.86°C., since all these 1 molal solutions contain the same number of solute molecules. With other solvents, the extent of lowering of the freezing temperature is different, but definite.

A familiar application of this lowering of the freezing temperature of liquids is found in the use of antifreeze mixture in automobile radiators. Alcohol, glycerol, ethylene glycol, etc., mixed with water

produce solutions having freezing temperatures lower than that of pure water.

Freezing Mixtures. Advantage of lowering in freezing temperature is also taken in the production of low temperatures required for a variety of purposes. Salt added to ice at 0°C. dissolves in the thin layer of liquid surrounding each piece of solid ice. The resulting solution has a vapor pressure less than that of the ice; hence, some ice will melt. Of course this melting is accompanied by an absorption of heat and if the ice is so insulated that it cannot absorb heat from its surroundings the heat is absorbed from the ice itself. Accordingly, the temperature of the mixture falls. A mixture of ice and sodium chloride will produce a temperature of −22°C., while ice and crystalline calcium chloride provide temperatures as low as −56°C.

10.4. Osmosis

Another important behavior exhibited by solutions is the phenomenon of *osmosis*. Certain membranes, notably the lining of eggshells, fish bladder, parchment paper, or even purely inorganic jellies such as copper ferrocyanide, or copper silicate, are of such character that certain kinds of molecules are capable of passing through these membranes, while other kinds of molecules cannot. A membrane that is permeable by one kind of molecule and not by another is called a *semipermeable* membrane. Frequently, it is found that such membranes are permeable by solvent but not permeable by solute molecules. When a solution of sugar in water is enclosed in a bag made of one of these membranes, or enclosed in a porous earthenware cup the pores of which are filled with an inorganic jelly such as copper ferrocyanide (Fig. 46), and the bag or cup is immersed in a less concentrated solution of sugar or in pure water, it will be observed that water passes into the bag or cup. This indicates that there is a net transfer of water molecules from the more dilute sugar solution or from the pure water into the more concentrated solution enclosed by the semipermeable membrane. This means that water molecules move from the region where the concentration of water molecules is greater (the dilute sugar solution or

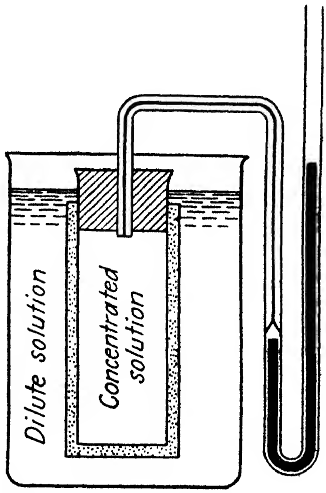


Fig. 46.—Osmotic-pressure cell.

pure water) to the region containing a lower concentration of water molecules (the concentrated sugar solution). Water molecules also move in the opposite direction but at a lesser rate. **The passage of solvent through a semipermeable membrane from a region of greater solvent concentration into a region of lower solvent concentration is called osmosis.**

The semipermeable membrane is free from holes, but it allows water and not sugar molecules to pass through it. Such substances take up water and swell when in contact with pure water and lose water and shrink when put in contact with solutions.

Osmotic Pressure. In an experiment utilizing an apparatus of the type shown in Fig. 46, water will pass from the beaker into the cell. This results in an increase in the volume of the sugar solution contained within the cell. By submitting the solution in the cell to an increase in pressure, this net transfer of solvent molecules may be prevented. The pressure that is just sufficient to prevent a net transfer of solvent molecules into the solution is termed the *osmotic pressure* of the solution. The magnitude of this pressure is proportional to (*a*) the concentration of solute molecules and (*b*) the absolute temperature. For a 1 molal solution of sugar, the osmotic pressure at 0° amounts to approximately 22.4 atm., and since the osmotic pressure is proportional to the absolute temperature, the osmotic pressure at 25°C. is approximately

$$22.4 \times {}^{298}\!/_{273} = 24.5 \text{ atm.}$$

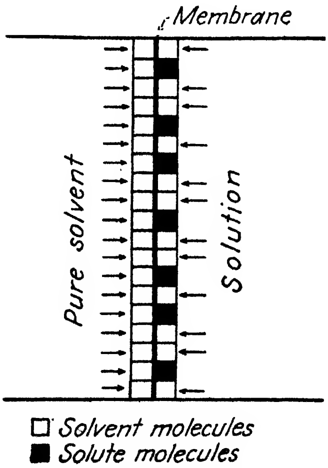


FIG. 47.—Diagram illustrating the relative number of impacts by solvent molecules on either side of a semipermeable membrane.

The mechanism by which osmosis occurs may be explained in much the same manner as the lowering of the vapor pressure. The rate of absorption of water by the membrane is proportional to the number of impacts by water molecules per unit of area per unit of time. Initially, the number of impacts is greater on the side exposed to pure water than on the side exposed to the sugar solution. This is true because (1) the concentration of water molecules is greater on that side and (2) on the side exposed to the solution, a part of the surface of the membrane is covered by sugar molecules (Fig. 47). Consequently, the rate of absorption of water is greater on the side exposed to pure water and there is a resultant net transfer of solvent into the solution.

Water molecules move into the solution in greater number per unit time than water molecules move out of the solution. When, however, the solution is put under pressure (or pressure is built up hydrostatically owing to the increase in the volume of the solution), the concentration of water molecules is increased in the solution; the unoccupied space between molecules is lessened by compression. If the applied pressure is sufficient, the rate of absorption of water molecules on the side of the membrane exposed to the solution may be made equal to the rate of absorption on the side exposed to pure water. The rates of transfer of water molecules in the two directions will be equal, a condition of dynamic equilibrium will exist, and there will be no net transfer of solvent molecules.

Applications of Osmosis. Solutions that exhibit the same osmotic pressure would exist in equilibrium when placed on opposite sides of a semipermeable membrane. The term *isotonic* is usually applied to solutions that have the same osmotic pressure. When solutions are injected into the blood stream either for purposes of medication or to replace blood that has been lost, the solution injected and the blood must be isotonic. Pure water injected into the blood stream in any appreciable quantity will prove fatal since water molecules would pass out of the blood stream and into the surrounding tissues and even into the corpuscles. Osmosis is of tremendous importance in biology, medicine, and other related sciences. The germination of seeds, the rise of sap into the branches and leaves of trees, and the nutrition of both plants and animals are only a few of the many common occurrences that involve the phenomenon of osmosis.

Some membranes are permeable not only to solvent molecules but also to certain kinds (but not all kinds) of solute molecules. It is through this selective action of membranes that the fluid in the stomach is acidified. A similar behavior is involved in the extraction of sugar from sugar beets. If the sliced beets are placed in a vessel through which a steady flow of pure water is maintained, the sugar passes through the cell walls of the beet and into the surrounding water while the other constituents of the beet are, in the main, not capable of permeating the cell wall. The explanation of this phenomenon may lie in the difference in size of the solute particles; the membrane may be permeable to particles of molecular size and not to particles of colloidal size.

10.5. Determination of Molecular Weights of Liquids and Solids

It was indicated in Sec. 7.8 that a knowledge of the properties of solutions provides a basis for the experimental measurement of the

relative weights of molecules of liquids and solids. The two properties most commonly utilized in this connection are the lowering of the freezing temperature and the elevation of the boiling temperature. It has been emphasized repeatedly that the properties of solutions are dependent upon the number of solute molecules present. One mole of sugar containing 6.02×10^{23} molecules dissolved in 1000 g. of benzene lowers the freezing temperature 5.12° and raises the boiling temperature 2.57°. Accordingly, if one measures the extent to which the boiling temperature or freezing temperature of a given weight of benzene is changed by the presence of a known weight of solute, the molecular weight of the solute may be calculated by comparison with the known behavior of sugar. Before specific examples are considered, it should be pointed out that the substances used here for purposes of illustration are chosen at random and that many other solutes and solvents could be employed equally well. Further, it should be indicated that this application requires that the solute dissolve in the solvent without the occurrence of any chemical change that would affect the relative weights of the solute molecules.

Fifty grams of pure benzene was found to freeze at 5.50°C. The addition of 1.5 g. of a pure solute lowered the freezing temperature to 3.86°C. The presence of 1.5 g. of solute therefore resulted in a lowering amounting to $5.50 - 3.86 = 1.64°$. The molecular weight of this solute is that weight which would lower the freezing temperature of 1000 g. of benzene 5.12° and may be calculated as follows:

Wt. of solute in 50 g. benzene = 1.5 g.
Wt. of solute in 1000 g. of benzene = $1.5 \times {}^{1000}\!/_{50} = 30$ g.
Freezing temperature lowering produced by 30 g. solute in 1000 g. benzene = $5.50 - 3.86 = 1.64°$
Freezing temperature lowering produced by 1 gram-molecular weight of solute in 1000 g. benzene = 5.12°

Hence, by simple proportion,

$$\text{Mol. wt. of solute} : 5.12 :: 30 : 1.64$$

$$\text{Mol. wt. of solute} = 30 \times \frac{5.12}{1.64} = 93.6$$

With the boiling temperature elevation method, the 50 g. of pure benzene was found to boil at 80.20°C., and the addition of 1.5 g. of solute produced a solution that boiled at 81.02°, or an elevation amounting to 0.82°C. Given the additional information that the presence of 1 gram-molecular weight of the solute in 1000 g. of benzene

would result in a boiling temperature elevation amounting to 2.57°, one may calculate the molecular weight of the solute.

$$\text{Wt. of solute in 50 g. benzene} = 1.5 \text{ g.}$$
$$\text{Wt. of solute in 1000 g. benzene} = 1.5 \times {}^{1000}\!/\!_{50} = 30 \text{ g.}$$

Boiling temperature elevation produced by 30 g. solute in 1000 g. benzene $= 81.02 - 80.20 = 0.82°$

Boiling temperature elevation produced by 1 gram-molecular weight of solute in 1000 g. benzene $= 2.57°$

Hence,

$$\text{Mol. wt. of solute} : 2.57 :: 30 : 0.82$$
$$\text{Mol. wt. of solute} = \frac{2.57 \times 30}{0.82} = 94.0$$

This value, allowing for experimental errors in either set of data, agrees very well with the value of 93.6 obtained by the method involving the lowering of the freezing temperature.

10.6. Solvation

The regularities observed in the influence of many solutes upon the physical properties of pure solvents are not realized if the solute undergoes chemical change upon being dissolved in a pure solvent. The kinds of chemical change that may occur are of several different types. The solute molecule may *dissociate* to form smaller units of matter or it may *associate* either with other solute molecules or with solvent molecules to form larger units.

If solute molecules (or atoms, or ions) become associated with molecules of the solvent, they are said to be *solvated* and this variety of chemical reaction is known as *solvation*. The extent of solvation depends upon the nature of the solute, the nature of the solvent, the temperature, etc. When commercial "soda ash" [sodium carbonate (Na_2CO_3)] is dissolved in water, extensive solvation occurs. Since water is the solvent most generally used, solvation by water is given the special name, *hydration*, and the substance formed by the union of, *e.g.*, Na_2CO_3 with water molecules is called a *hydrate*. If a saturated solution of Na_2CO_3 in water is cooled or if the solvent is allowed to evaporate slowly, the crystals that separate from the solution are found to have the composition represented by the formula $Na_2CO_3 \cdot 10H_2O$. This does not prove that the Na_2CO_3 may not have been associated with more than $10H_2O$ *in the solution*. The number of water molecules may have been greater than but probably not less than 10. Solvent that actually separates in combination with the solute in crystalline form is known as *solvent of crystallization;* in the

above case, *water of crystallization*. Thus, a distinction is made between association in solution and association in the crystal. Other examples of salt hydrates are $CuSO_4 \cdot 5H_2O$, $CdCl_2 \cdot 2H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Fe_3(PO_4)_2 \cdot 8H_2O$.

Efflorescence. Many salts containing water of crystallization are somewhat unstable under ordinary atmospheric conditions. Because the crystals contain combined water, the crystal exerts (at any given temperature) a definite water vapor pressure. If the water vapor pressure of the crystal happens to be greater than the partial pressure of water vapor in the atmosphere, the crystal will lose water to the surrounding atmosphere. This behavior is known as *efflorescence*. Thus, when $Na_2CO_3 \cdot 10H_2O$ is exposed to dry air, the hydrate loses water of crystallization and is changed to a white powder. When the partial pressure of water vapor in the atmosphere is sufficiently great, dry salts are frequently capable of taking water from the atmosphere (Sec. 10.1).

Salts which contain water of crystallization and which exert a water vapor pressure equal to or greater than that of the surrounding atmosphere may be caused to lose water if the vapor pressure is increased by the application of heat. Sometimes this loss of water by the crystal occurs in a stepwise manner as the temperature is increased. For example,

$$CuSO_4 \cdot 5H_2O + \text{heat} \xrightarrow{110^\circ} CuSO_4 \cdot H_2O + 4H_2O$$

$$CuSO_4 \cdot H_2O + \text{heat} \xrightarrow{230^\circ} CuSO_4 + H_2O$$

EXERCISES

1. Define the following terms: (*a*) osmosis, (*b*) osmotic pressure, (*c*) semipermeable membrane, (*d*) isotonic solutions.

2. Distinguish clearly between (*a*) water of hydration and water of crystallization, (*b*) hydration and solvation, (*c*) efflorescence and deliquescence.

3. In ascending a mountain road, the operating temperature of an automobile motor did not increase but the water in the radiator boiled as the automobile approached the summit of a particularly high mountain. Another identical automobile operating at the same motor temperature but containing an antifreeze mixture in the radiator reached the top of the same mountain without boiling the solution in the radiator. (*a*) Why did the water boil in the radiator of the first automobile? (*b*) How can one account for the fact that, under the same conditions, the solution in the radiator of the second automobile did not boil?

4. An antifreeze mixture *A* was prepared by dissolving 1 gal. of ordinary alcohol (C_2H_6O) in 5 gal. of water. Another mixture *B* was made by dissolving 1 gal. of "wood alcohol" (CH_4O) also in 5 gal. of water. During a cold period, mixture *A* froze and mixture *B* did not. Explain.

5. A solution consisting of 4 g. of a pure solute dissolved in 100 g. of pure water was found by experiment to freeze at a temperature of $-0.98°C$. Calculate the molecular weight of the solute.

6. Pure carbon tetrachloride boils at 76.80°C. and a 1 *m* solution of a nonvolatile solute in carbon tetrachloride boils at 81.68°. In a molecular weight determination, 3.6 g. of a pure solute dissolved in 88.4 g. of pure carbon tetrachloride formed a solution which boiled at 80.32°. Calculate the molecular weight of the solute.

7. An attempt was made to determine the molecular weight of a salt by measuring the elevation of the boiling temperature of pure water. The molecular weight of this salt was already known to be approximately 106. However, the molecular weight values obtained by experiment were always much too high. Suggest an explanation for these results.

8. Of two clear liquids, one is known to be a solution and the other the corresponding pure solvent. Without altering the concentration of the solution in any way, how could one determine which of the two is the solution?

SUGGESTED READING

Journal of Chemical Education

STEINBACH, Laboratory Experiments on Deliquescence and Efflorescence, **20,** 146 (1943).

DAVIDSON, A Simple Presentation of the Concepts of Osmosis, Osmotic Pressure, and Osmotic Work, **11,** 499 (1934).

CHAPTER XI

ACIDS, BASES, AND SALTS; NOMENCLATURE

The study and practice of chemistry are greatly simplified if one can think in terms of *types* or kinds of chemical substances and reactions rather than always in terms of specific cases. For example, there are many compounds known as *oxides* but for most purposes it is not necessary that one become familiar with the detailed behavior of each such compound. Rather, it is desirable to recognize that oxides may be classified according to type and that all oxides of a given type have certain properties in common. Thereafter, a detailed knowledge of the properties of individual oxides may be acquired as needed. The initial problem involved in the study of those classes of compounds known as *acids*, *bases*, and *salts*, therefore, is that of becoming acquainted with the chemical behavior characteristic of these types of compound. In addition, it is necessary that the student acquire a somewhat more detailed knowledge of a few common representatives of each class.

11.1. Acids

It has already been indicated that acids are compounds containing hydrogen which may be replaced (at least in part) by certain metals. In addition, there are other properties that are exhibited by those acids which are soluble in water. In general, water solutions of acids have a sour taste and have the ability to bring about changes in the colors of certain dyes. When it is brought into the presence of an acid, the blue form of the dye known as *litmus* is changed into a form that exhibits a red coloration. It is well to recognize at the outset that those properties which are thought of as being characteristic of acids are really the properties of water solutions of the compounds called *acids* and not so much the properties of the pure compounds themselves.

In the following paragraphs, some common acids are considered under headings that are related to the elemental complexity of the compounds involved. If the molecules of compounds contain two kinds of elements, the compounds are classed as *binary*. Similarly, *ternary* compounds are those consisting of molecules made up of three kinds of elements. (The use of the terms *binary* and *ternary* is by no means restricted to acids.)

Binary Acids. The names of four common compounds, their formulas, and the names applied to their solutions in water (which exhibit acidic properties) are listed in Table 12.

TABLE 12
COMMON BINARY ACIDS

Compound	Formula	Name of water solution
Hydrogen chloride	HCl	Hydrochloric acid
Hydrogen bromide	HBr	Hydrobromic acid
Hydrogen iodide	HI	Hydriodic acid
Hydrogen sulfide	H_2S	Hydrosulfuric acid

When dissolved in water, these compounds form solutions that exhibit acidic properties. Thus, pure gaseous hydrogen chloride does not exhibit acidic properties, but a water solution of hydrogen chloride is known as *hydrochloric acid.* Binary acids are composed of hydrogen and a nonmetal, but it must be borne in mind that not all such compounds are acids.

Ternary Acids. The ternary acids *may be* formed by the combination of oxides of nonmetals with water. The following equations serve to illustrate the formation of the common ternary acids:

$$\underset{\text{Sulfur trioxide}}{SO_3} + H_2O \rightarrow \underset{\text{Sulfuric acid}}{H_2SO_4}$$

$$\underset{\text{Sulfur dioxide}}{SO_2} + H_2O \rightarrow \underset{\text{Sulfurous acid}}{H_2SO_3}$$

$$\underset{\text{Nitrogen pentoxide}}{N_2O_5} + H_2O \rightarrow \underset{\text{Nitric acid}}{2HNO_3}$$

$$\underset{\text{Phosphorus pentoxide}}{P_2O_5} + 3H_2O \rightarrow \underset{\text{Phosphoric acid}}{2H_3PO_4}$$

$$\underset{\text{Phosphorus trioxide}}{P_2O_3} + 3H_2O \rightarrow \underset{\text{Phosphorous acid}}{2H_3PO_3}$$

$$\underset{\text{Carbon dioxide}}{CO_2} + H_2O \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

Another common ternary acid is that known as *acetic acid* ($HC_2H_3O_2$). It is not formed in any manner similar to that given for the other common ternary acids and differs from them also in that only one of the four hydrogen atoms may be replaced by metals, a fact that is emphasized by the manner in which the formula is written.

Acid Anhydrides. An inspection of the equations given above suggests a clear-cut relationship between certain nonmetal oxides and certain acids. For example, SO_3 is related to sulfuric acid, and P_2O_3 is related to phosphorous acid in the same sense. **Any nonmetal**

oxide that reacts with water to form an acid is called an acid anhydride. Thus, N_2O_5 is the anhydride of nitric acid, SO_2 is the anhydride of sulfurous acid, etc. Literally, the term *anhydride* means "without water."

11.2. Bases

Just as hydrogen is the characteristic component of all acids, so the hydroxyl radical (OH) is the characteristic component of many but not all bases. Bases in water solution have a bitter taste, have a "soapy" feel, and produce an irritant effect upon the skin. Solutions of bases change the colors of certain dyes, and the color changes produced by bases are usually the reverse of the changes produced by acidic solutions. Thus, bases change the color of litmus from red to blue. There are many bases, however, that do not exhibit these properties because of their insolubility in water. In fact, only a few of the common bases are appreciably soluble in water.

Hydroxides are ternary compounds some of which may be formed directly by the union of oxides of metals with water. Still other bases such as NH_4OH arise by the reaction of other types of compound with water. The following equations serve to illustrate the formation of a number of common bases which are measurably soluble in water:

$$\underset{\text{Sodium oxide}}{Na_2O} + H_2O \rightarrow \underset{\text{Sodium hydroxide}}{2NaOH}$$

$$\underset{\text{Potassium oxide}}{K_2O} + H_2O \rightarrow \underset{\text{Potassium hydroxide}}{2KOH}$$

$$\underset{\text{Calcium oxide}}{CaO} + H_2O \rightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2}$$

$$\underset{\text{Barium oxide}}{BaO} + H_2O \rightarrow \underset{\text{Barium hydroxide}}{Ba(OH)_2}$$

$$\underset{\text{Ammonia}}{NH_3} + H_2O \rightarrow \underset{\text{Ammonium hydroxide}}{NH_4OH}$$

The compound ferric hydroxide [$Fe(OH)_3$] is a typical example of an insoluble base. It might be suggested that $Fe(OH)_3$ might be formed by the union of iron oxide (Fe_2O_3) and water.

$$Fe_2O_3 + 3H_2O \rightarrow 2Fe(OH)_3$$

When Fe_2O_3 is added to water, however, this reaction does not occur to any marked extent because the insoluble particles of Fe_2O_3 quickly become coated with insoluble $Fe(OH)_3$ and this coating effectively protects the remaining Fe_2O_3 from coming into contact with the water required for continuation of the reaction. Obviously then, if one wished to prepare $Fe(OH)_3$, it would be necessary to use some less

direct method. As a general rule, only the soluble bases may be formed in appreciable quantity by the reaction of metal oxides and water.

Basic Oxides. By comparison with acid anhydrides, it might appear that the oxides of the metals could be looked upon as base anhydrides. This is seldom done because so few metal oxides actually react with water to form the corresponding bases. The metal oxides are sometimes called *basic oxides*, or simply *bases*. Even though an oxide may not react with water to form the corresponding base, the oxide and the base may be considered as being related in a purely formal way.

11.3. Neutralization

If a given volume of a 1 *M* solution of hydrochloric acid is mixed with the same volume of a 1 *M* solution of sodium hydroxide, the resulting solution will have neither the properties of an acid nor the properties of a base; it is therefore said to be *neutral*. If this neutral solution is evaporated to dryness, the only solid product remaining will be found to be sodium chloride. The equation for the reaction is

$$HCl + NaOH \rightarrow H_2O + NaCl$$

Other acids and bases react similarly, *e.g.*,

$$H_2SO_4 + 2NaOH \rightarrow 2H_2O + Na_2SO_4$$
$$2H_3PO_4 + 3Ca(OH)_2 \rightarrow 6H_2O + Ca_3(PO_4)_2$$

In every reaction of this kind, the products are water and a salt, and it should be recognized that, whereas the identity of the salt is dependent upon the acid and base employed, *water is produced in every case.* **The formation of water** (and a salt) **by the interaction of an acid and a base is known as neutralization.** Even the insoluble bases react with acids provided the salt produced is soluble, thus,

$$3HCl + Fe(OH)_3 \rightarrow 3H_2O + FeCl_3$$

The insoluble oxide Fe_2O_3 does not react extensively with water but is dissolved readily in acids, probably because the acid neutralizes the protective coating of $Fe(OH)_3$ on the surface of the insoluble oxide and thus permits further reaction between it and water.

That the essential reaction involved in neutralization is the formation of water may be shown by a study of the energy changes involved. Reactions of neutralization are exothermal. If one measures the heat evolved in a large number of neutralization reactions between dilute solutions of different acids and different bases, in every case the

quantity of heat evolved upon formation of 1 mole of water is found to be approximately 13,700 cal. This indicates that the heat of reaction is essentially independent of the nature of the salt produced and is related only to the formation of water from the hydrogen of the acid and the hydroxyl radical of the base.

Titration. The chemist frequently has need to determine the volume of one solution required to react with a given volume of another solution. This procedure is known as *titration*, and one is said to *titrate* the one solution against the other. For example, a titration involving a neutralization reaction may be carried out as follows: A known volume of a solution of a base is placed in a beaker and to this solution is added a few drops of a solution of litmus. If a solution of an acid is added from a burette (Fig. 48), the base will be neutralized by the acid but the color of the solution will remain blue as long as any of the base remains. Finally, when all of the base has been neutralized and a very slight excess of acid has been added, the color of the solution will change from blue to red. Because the color change is used to denote the end of the neutralization reaction, the dye is called an *indicator* and the occurrence of the color change is referred to as the *end point* of the titration. When one knows the concentration of the acid solution and the volume of acid solution required to neutralize a given volume of the base, the weight of base neutralized and the weights of water and salt formed in the reaction may be calculated.

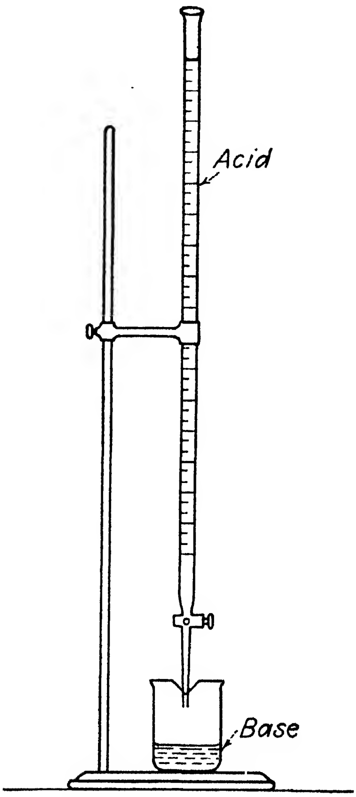


Fig. 48.—Titration.

11.4. Salts

The formation of salts has been shown to result from (1) reactions between metals and acids, (2) reactions between metals and bases, and (3) reactions between acids and bases. Salts constitute one of the most common and useful classes of chemical substances. Other

methods by means of which the formation of salts may be accomplished are (4) reactions between acid anhydrides and basic oxides, *e.g.*,

$$CO_2 + CaO \rightarrow CaCO_3$$

(5) reactions between salts and acids, *e.g.*,

$$2NaBr + H_2SO_4 \rightarrow 2HBr + Na_2SO_4$$

and (6) reactions between salts. This latter method is one of great importance and will be studied in more detail as the need for this information arises. The following is a typical example:

$$CaCl_2 + Na_2SO_4 \rightarrow CaSO_4 + 2NaCl$$

Here it is seen that two salts react to form two other salts.

Thus far, definitions of the terms *acid*, *base*, and *salt* have not been formulated. To define these terms (and for that matter the term *neutralization* as well) in a most satisfactory manner requires more information concerning the condition in which acids, bases, and salts exist in solution. The study of the theory of ionization (Chap. XVII) will provide the necessary information. In the meantime, the student should think of these classes of compounds in terms of their properties, their mode of formation, and in relation to reactions in which these substances participate.

NOMENCLATURE

Unfortunately the names assigned to chemical compounds often fail to conform to any consistent scheme of nomenclature. All too frequently, common or wholly trivial names, lacking in chemical significance, are employed. Ideally, the name of a compound should convey the information required to write the formula. The nomenclature of acids, bases, and salts is fairly consistent but the exceptions to the general rules of nomenclature are numerous.

11.5. Nomenclature of Binary Compounds

In general, the names of binary compounds (other than binary acids) are constructed from the names of the two elements involved. Since the symbol for the more metallic of the two elements is ordinarily written first in the formula, the name of that element logically is used as the first part of the name of the compound. The second part of the name of the compound consists of the stem of the name of the less metallic element together with the suffix, *-ide*. Thus, the compound

CaO has the systematic name calcium oxide [*i.e.*, calcium + (oxygen − ygen + ide)]. Similarly, the compound $PbCl_2$ is called lead chloride [*i.e.*, lead + (chlorine − ine + ide)].

In devising names for compounds of the nonmetals (and to some extent those of the metals as well) it often becomes necessary to indicate in the name of the compound the number of atoms of at least one variety of element present in the molecule. This may be done conveniently by the use of suitable prefixes. For example, the name carbon oxide is itself inadequate since it might refer equally well to CO or CO_2. Consequently, the names carbon *mon*oxide and carbon *di*oxide, respectively, are employed. Similarly, the compounds PCl_3 and PCl_5 are called phosphorous *tri*chloride and phosphorous *penta*chloride, respectively.

Particularly among binary compounds of the metals (and less frequently in the cases of certain compounds of the nonmetals) the names are so written as to indicate the valence state of the more metallic of the two elements. Such a scheme becomes necessary where two elements form more than one compound. For example, consider the case of the two compounds Hg_2O and HgO. In such cases, the names are formed by appending to the name of the more metallic element the suffix *-ous* in the case of the compound in which the more metallic element exhibits the lower valence and, to indicate the higher valence, the suffix *-ic* is appended similarly. Thus, Hg_2O is called mercur*ous* oxide and HgO is named mercur*ic* oxide. Similarly, $FeCl_2$ and $FeCl_3$ are called ferr*ous* chloride and ferr*ic* chloride, respectively.

It is indeed unfortunate that, in the past, chemists have not expended greater effort in the direction of systematization of nomenclature. There are very many exceptions to the foregoing rules. For example, the compound ammonia is almost always represented by an incorrectly written formula and an unsystematic name. Chemists, by habit, write the formula NH_3 and use the trivial name ammonia, whereas the formula should be written H_3N and the systematic name trihydrogen nitride should be employed.

11.6. Nomenclature of Bases

The naming of bases is a relatively simple matter. The name of a base is formed from the name of the metal (or the radical in the case of a base such as NH_4OH) together with the term *hydroxide*. Thus, NaOH is sodium hydroxide, $Cu(OH)_2$ is copper hydroxide, NH_4OH is ammonium hydroxide, etc. It is unfortunate that the names of these ternary compounds end in *-ide*, a suffix which otherwise is used only in the names of binary compounds.

11.7. Nomenclature of Acids

The scheme generally followed in naming acids is somewhat more involved and requires that distinction be made between binary and ternary acids.

Binary Acids. The names of binary acids consist of the prefix *hydro-*, all or part of the name of the nonmetal, and the suffix *-ic*. For example, the binary acid containing bromine (HBr) is hydrobromic acid (hydro + brom + ic); that containing sulfur (H_2S) is hydrosulfuric acid (hydro + sulfur + ic). The names for the other binary acids are derived similarly.

Ternary Acids. The naming of these acids is complicated by the fact that one nonmetal may be the key element in more than one ternary acid. In such cases, the name of the most common acid is formed from all or part of the name of the nonmetal together with suffix *-ic* (but without the prefix *hydro-*, which is used only in the names of binary acids). Common examples are

H_2SO_4, sulfuric acid (sulfur + ic)
$HClO_3$, chloric acid (chlor + ic)

and

HNO_3, nitric acid (nitr + ic)

Should there be corresponding acids containing one less atom of oxygen, the names are formed in the same manner but employ the suffix *-ous* in place of *-ic*, thus,

H_2SO_3, sulfurous acid (sulfur + ous)
$HClO_2$, chlorous acid (chlor + ous)

and

HNO_2, nitrous acid (nitr + ous)

This scheme is adequate unless still more acids containing the key element are known. In addition to $HClO_3$ and $HClO_2$, the acids having the formulas $HClO$ and $HClO_4$ also are known. It will be noted that $HClO_4$ contains 1 atom of oxygen *more than* the acid having a name ending in *-ic*. Accordingly, this is designated by appending the prefix *per-*, and the name of $HClO_4$ becomes perchloric acid (per + chlor + ic). Similarly, the acid $HClO$ contains 1 atom of oxygen *less than* does that having the name ending in *-ous*, and this information is incorporated in the name by using the prefix *hypo-*. Hence, the name is hypochlorous acid (hypo + chlor + ous).

11.8. Nomenclature of Salts

Salts are named in relation to the acids from which they may be derived. The names of binary salts consist of the name of the metal, the stem of the name of the nonmetal other than oxygen, and the suffix *-ide* (Sec. 11.5). On this basis, NaBr is called sodium bromide; AlF_3 is aluminum fluoride; CdS is cadmium sulfide, etc.

Ternary salts are assigned names which incorporate the name of the metal and which otherwise conform to the following rules: (1) If the name of the parent acid ends in *-ic*, the name of the salt must end with the suffix *-ate*. (2) If the name of the acid ends in *-ous*, the name of the salt must end with the suffix *-ite*. (3) If the name of the parent acid ends in *-ic* or *-ous* and involves a prefix such as *per-* or *hypo-*, the prefix is retained in the name of the salt. The application of these rules to the naming of the sodium salts derived from the four ternary acids of chlorine is shown in Table 13.

TABLE 13
NOMENCLATURE OF SALTS

Acid		Salt	
Formula	Name	Formula	Name
HClO	Hypochlorous acid	NaClO	Sodium hypochlorite
$HClO_2$	Chlorous acid	$NaClO_2$	Sodium chlorite
$HClO_3$	Chloric acid	$NaClO_3$	Sodium chlorate
$HClO_4$	Perchloric acid	$NaClO_4$	Sodium perchlorate

Another practice commonly encountered in the naming of salts is the use of the prefix *bi-*; *e.g.*, sodium bicarbonate ($NaHCO_3$). This prefix should not be used at all in the names of inorganic salts of the type represented by $NaHCO_3$, and a means of avoiding its use will be given elsewhere (Sec. 17.9).

11.9. An Improved System of Nomenclature

The need for a better system of naming inorganic compounds has long been recognized. This need was met in part in 1940 when a committee representing the chemists of several different countries recommended an improved system for the nomenclature of both simple and complex inorganic compounds. Since these rather extensive recommendations were made, there has been increasing evidence of general adoption and use of these particular rules.

Since a comprehensive discussion of the general problem of nomenclature is beyond the scope of this book, the present discussion will be limited to the new scheme for the naming of simple binary and ternary compounds.

Certain types of simple binary compounds are named in a manner such that the number of each kind of atom in the molecule is designated by Greek numerical prefixes in all cases except that in which the number is one. The names given below for the oxides of nitrogen serve to illustrate the method and show that the formula may be written directly on the basis of the systematic name.

Name	Formula
Dinitrogen oxide	N_2O
Nitrogen oxide	NO
Dinitrogen trioxide	N_2O_3
Nitrogen dioxide	NO_2
Dinitrogen tetroxide	N_2O_4
Dinitrogen pentoxide	N_2O_5

Other simple binary compounds may be named similarly, and many of the names already in use conform to this system, *e.g.*, carbon monoxide, carbon dioxide, iron disulfide, etc. Ternary compounds may be named similarly, provided they are composed of one element and a radical having an established name.

Certain other types of binary, ternary, and quaternary compounds are given names that include designations of valence wherever necessary, *i.e.*, elements that exhibit more than one valence. The valence is shown by Roman numerals placed in parentheses immediately following the name of the element in question. The accompanying formulas and the corresponding systematic names will serve as illustrations.

Formula	Name
FeO	Iron (II) oxide
Fe_2O_3	Iron (III) oxide
Fe_3O_4*	Iron (II,III) oxide
$CrCl_3$	Chromium (III) chloride
$Hg(NO_3)_2$	Mercury (II) nitrate
$Pb(C_2H_3O_2)_4$	Lead (IV) acetate

* This formula may also be written as $FeO \cdot Fe_2O_3$.

It is not necessary to designate the valence of elements that seldom exhibit more than one valence, *e.g.*, Al, Zn, Ca, Na, K, etc.

It will be noted that the foregoing examples do not involve the use of suffixes such as *-ous* and *-ic*. According to this system of nomenclature, these and similar suffixes are not used except in the naming of acids.

In the remainder of this book, only infrequent reference will be made to this system of nomenclature. However, it is felt that the student should be aware of the fact that inorganic nomenclature is presently undergoing a transition to more systematic practices. This is particularly important for those students who expect to continue with the study of chemistry.

11.10. Quantitative Aspects of Neutralization

One liter of 1 *M* (or 1 *m*) hydrochloric acid solution will neutralize 1 liter of 1 *M* (or 1 *m*) sodium hydroxide solution because the two solutions contain solutes (HCl and NaOH, respectively) in the quantities required by the following equation:

$$\underset{36.5\text{ g.}}{HCl} + \underset{40\text{ g.}}{NaOH} \rightarrow H_2O + NaCl$$

That is, the neutralization reaction is not a reaction of the solution as such, but rather is one that depends upon the identity and properties of the solutes. Reactions of neutralization occur in relation to the H and OH content of the acidic and basic solutions, respectively. Accordingly, molar and molal solutions are not convenient standard solutions for use in reactions of neutralization. For example, 1 liter of a 1 *M* solution of H_2SO_4 contains 2.016 g. of replaceable H and can therefore neutralize 2 liters of 1 *M* sodium hydroxide solution, each liter of which contains 17.008 g. of OH, since

$$\underset{1.008\text{ g.}}{H} + \underset{17.008\text{ g.}}{OH} \rightarrow \underset{18.016\text{ g.}}{H_2O}$$

This situation suggests a need for a kind of standard solution which is related directly to the particular chemical individuals involved in the fundamental chemical changes in which these solutions are to be employed. *Normal solutions* are defined, prepared, and used in accordance with this point of view.

Normal Solutions of Acids. A normal solution of an acid is one that contains 1 gram atom of replaceable hydrogen (1.008 g.) per liter of solution. On this basis, a specified volume of a 1 *N* solution of *any* acid will contain the same weight of replaceable hydrogen as the same volume of 1 *N* solution of any other acid. This relation may be clarified by consideration of the following examples. Suppose that it is desired to prepare 1 liter of 1 *N* solution of each of the acids, HCl, H_2SO_4, and H_3PO_4. The weight of solute required in each case is

(*a*) HCl: Mol. wt. = 36.465 g., of which 1.008 g. is hydrogen. Consequently, 36.465 g. of HCl dissolved in enough water to make 1

liter of solution will provide a solution containing the exact weight of replaceable H required by the definition of a normal solution of an acid.

(*b*) H_2SO_4: Mol. wt. = 98.076 g. containing 2.016 g. of replaceable hydrogen. If 98.076 g. of H_2SO_4 were dissolved in enough water to make 1 liter of solution, the resulting solution would be 2 N since it would contain 2 gram atoms of replaceable hydrogen. Accordingly, 98.076 ÷ 2 = 49.038 g. of H_2SO_4 is the required weight of solute per liter of 1 N solution of sulfuric acid.

(*c*) H_3PO_4: Mol. wt. = 98.044 g. Since 1 gram-molecular weight of H_3PO_4 contains 3 gram atoms of replaceable hydrogen, the weight of H_3PO_4 required to prepare 1 liter of 1 N phosphoric acid solution is 98.044 ÷ 3 = 32.682 g.

Normal Solutions of Bases. A normal solution of a base is one that contains 17.008 g. of available hydroxyl (OH) per liter of solution. In terms of this definition, the weights of potassium hydroxide and barium hydroxide required to prepare one liter of 1 N solutions are

(*a*) KOH: Mol. wt. = 56.104 g. Of this weight, 17.008 g. are contributed by the one OH radical. Hence, 56.104 g. of KOH dissolved in enough water to make 1 liter of solution will provide a 1 N solution of potassium hydroxide.

(*b*) $Ba(OH)_2$: Mol. wt. = 171.376 g., containing a total of 2 × 17.008 g. of OH. Hence, 171.376 ÷ 2 = 85.688 g. is the weight of $Ba(OH)_2$ required to prepare 1 liter of 1 N barium hydroxide solution.[1]

Equivalence of Normal Solutions of Acids and Bases. By virtue of the manner in which these solutions are prepared, any given volume of any 1 N acid solution is chemically equivalent to the same volume of any 1 N solution of a base. For example, 50 ml. of a 1 N solution of *any* acid contains just exactly the quantity of H required to neutralize the weight of OH contained in 50 ml. of a 1 N solution of *any* base. If the acid solution is 2 N, then 50 ml. of 2 N acid will neutralize 100 ml. of 1 N base. A little reflection will serve to show the correctness of the following relationship:

$$N_{(\text{acid})} \times V_{(\text{acid})} = N_{(\text{base})} \times V_{(\text{base})}$$

where N and V represent normality and volume, respectively.

Normal Solutions of Salts. Although in common use, normal solutions of salts are relatively less important than normal solutions of acids and bases and, for this reason, will not be considered in detail

[1] In fact, barium hydroxide is not sufficiently soluble in water to permit the preparation of a 1 N solution of this base. However, solutions of lower normality (up to about 0.4 N) are possible and are used extensively.

here. Normal solutions of salts are prepared in relation to the particular constituent (atom or radical) which is to be involved in the reactions in which the salt solution is to participate.

Preparation of Normal Solutions. Since solutions that are 1 *N* are usually too concentrated for most purposes, it is more suitable to prepare 0.5 *N*, 0.1 *N*, 0.01 *N* or solutions of any convenient normality. In order to illustrate the procedure involved in the preparation of a given volume of a solution of some specified normality, suppose that one requires 700 ml. of 0.2 *N* sulfuric acid solution. The first problem is that of calculating the weight of pure hydrogen sulfate required.

1 liter of 1 *N* sulfuric acid solution requires $98.076/2 = 49.038$ g. H_2SO_4

1 liter of 0.2 *N* sulfuric acid solution requires $49.038 \times 0.2 = 9.8076$ g. H_2SO_4

700 ml. of 0.2 *N* sulfuric acid solution requires $9.8076 \times {}^{700}\!/_{1000} = 6.8653$ g. H_2SO_4

Next, one would weigh out exactly 6.8653 g. of pure H_2SO_4, dissolve it in water contained in a flask of suitable size, then add just enough water to make a total volume of exactly 700 ml. of solution.

EXERCISES

1. Define the following terms: (*a*) acid anhydride, (*b*) neutralization, (*c*) titration, (*d*) indicator, (*e*) end point.

2. What is the formula of the anhydride of chromic acid (H_2CrO_4), of arsenic acid (H_3AsO_4), of perchloric acid?

3. Show by means of an equation that chlorine dioxide (ClO_2) is at the same time the anhydride of both chlorous and chloric acids.

4. Write equations to represent the reactions that occur between the following:

(*a*) Calcium hydroxide and sulfuric acid
(*b*) Bismuth hydroxide and hydrochloric acid
(*c*) Magnesium hydroxide and acetic acid
(*d*) Lead hydroxide and phosphoric acid
(*e*) Zinc hydroxide and hydrobromic acid
(*f*) Potassium hydroxide and hydriodic acid
(*g*) Barium hydroxide and chloric acid

5. Write systematic names for each of the following simple binary compounds:

(*a*) SCl_2
(*b*) P_2O_5
(*c*) $SiBr_4$
(*d*) PbO_2
(*e*) Na_2S_4
(*f*) As_2O_3

6. Of the following known oxides of nitrogen, N_2O is commonly called nitrous oxide and NO is known as nitric oxide. Assuming, however, that the suffixes *-ous* and *-ic* are not to be used at all, assign suitable systematic names for the following: N_2O, NO, NO_2, NO_3, N_2O_3, N_2O_5.

7. From the following names, write the corresponding formulas:

(a) Dipotassium tetroxide
(b) Stannous iodide
(c) Plumbous oxide
(d) Mercuric sulfide
(e) Silicon dioxide

8. Write systematic names for each of the following salts:

$BiBr_3$	$Al_2(SO_4)_3$	$AgClO_4$
Na_2SO_4	$Cu(NO_2)_2$	$Cd_3(PO_4)_2$
$Zn(ClO_3)_2$	FeI_3	$Mn(NO_3)_2$
$KClO_2$	$Ca(ClO)_2$	$Sn(PO_3)_2$

9. From the following systematic names, write the formulas for the following salts:

Nickel sulfate	Strontium fluoride
Barium chlorite	Magnesium perchlorate
Lead acetate	Zinc phosphate
Sodium phosphite	Silver hypochlorite

10. What is the normality of (a) 1 M sulfuric acid solution, (b) 0.5 M sodium hydroxide solution, (c) 2 M phosphoric acid solution?

11. Find the weight of solute required to prepare the following solutions:

(a) 2 liters of 0.1 N phosphoric acid solution
(b) 500 ml. of 4 N potassium hydroxide solution
(c) 200 ml. of 0.06 N perchloric acid solution
(d) 8 liters of 0.8 N hydrobromic acid solution

12. Find the weight of solute contained in each of the following solutions:

(a) 1 liter of 0.2 N hypochlorous acid solution
(b) 16 liters of 0.003 N ammonium hydroxide solution
(c) 50 ml. of 6 N sulfuric acid solution
(d) 1 ml. of 0.75 N hydriodic acid solution

13. In a titration, 26 ml. of 0.4 N sulfuric acid solution was required exactly to neutralize 38 ml. of a barium hydroxide solution.

(a) Calculate the *weight* of $Ba(OH)_2$ contained in the 38 ml. of barium hydroxide solution.

(b) Using *only* the weight of solute (calculated above) and the volume of 38 ml., calculate the normality of the barium hydroxide solution.

(c) Calculate the normality of the barium hydroxide solution using the relationship given in Sec. 11.10.

14. What volume of 0.001 N hydrosulfuric acid solution would be equivalent to 0.66 ml. of 0.024 N hydrobromic acid solution?

15. What volume of water must be added to 112 ml. of 0.18 N hydrochloric acid solution in order to lower the normality to 0.0075?

16. A lump of solid pure calcium oxide was placed in water and neutralized by the addition of 60 ml. of 2.4 N hydrochloric acid solution. Without the use of any typical calculations based upon chemical equations, calculate the *weight* of the lump of calcium oxide.

SUGGESTED READING

Journal of Chemical Education

Beezer, Latin and Greek Roots in Chemical Terminology, **17**, 63 (1940).

Ewing, What's in a Name?, **15**, 123 (1938).

Seidell, Limitations upon the Unification of Chemical Nomenclature, **6**, 720 (1929).

Chemical Reviews

Scott, The Need for Reform in Inorganic Chemical Nomenclature, **32**, 73 (1943).

Journal of the American Chemical Society

Jorissen, Bassett, Damiens, Fichter, and Remy, Rules for Naming Inorganic Compounds, **63**, 889 (1941).

See also references at end of Chap. XX.

CHAPTER XII

REVERSIBLE REACTIONS AND CHEMICAL EQUILIBRIUM

The idea of two processes occurring simultaneously but in opposite directions is not a new one. Such related processes have been seen to be involved when a volatile liquid such as water is in contact with water vapor in a closed vessel (Sec. 6.5),

$$H_2O_{(liquid)} \rightarrow H_2O_{(vapor)}$$

while, at the same time,

$$H_2O_{(vapor)} \rightarrow H_2O_{(liquid)}$$

Similarly, when a saturated solution of sugar exists in contact with undissolved solute (Sec. 9.4),

$$C_{12}H_{22}O_{11(solid)} \rightarrow C_{12}H_{22}O_{11(dissolved)}$$

and

$$C_{12}H_{22}O_{11(dissolved)} \rightarrow C_{12}H_{22}O_{11(solid)}$$

These processes may be represented each by a single expression,

$$H_2O_{(liquid)} \rightleftharpoons H_2O_{(vapor)}$$
$$C_{12}H_{22}O_{11(solid)} \rightleftharpoons C_{12}H_{22}O_{11\ (dissolved)}$$

Here the double arrows simply indicate that the conversion of liquid water to water vapor and the change from solid sugar to dissolved sugar are reversible processes. Although these two examples are concerned entirely with physical changes, they suggest that similar situations may be anticipated among chemical transformations.

12.1. Reversible Reactions

In Sec. 3.3, the formation of water was represented by the equation,

$$2\overline{H}_2 + \overline{O}_2 \rightarrow 2H_2O$$

In Secs. 4.1 and 8.5, the decomposition of water was given as a method for the preparation of oxygen and hydrogen, respectively.

$$2H_2O \rightarrow 2\overline{H}_2 + \overline{O}_2$$

These two equations may be combined into a single expression,

$$2\overline{H}_2 + \overline{O}_2 \rightleftharpoons 2H_2O$$

which provides the information that the union of hydrogen and oxygen is a reversible chemical reaction and that the formation and decomposition of water may occur at the same time. If the rate of formation of water is the same as the rate of decomposition, the two chemical reactions exhibit that balance of opposing tendencies which is known as a *state of dynamic equilibrium.*

Another example of a reversible reaction has been encountered previously. The formation of hydrogen by the reaction,

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

and the "reduction" of magnetic oxide of iron by means of hydrogen,

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

are also seen to constitute a reversible system which may be represented by the single equation,

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

A reversible chemical reaction is one that is capable of proceeding in either of two directions. In referring to systems of this sort, the chemist speaks of the reaction represented by the arrow pointing toward the right as "the forward reaction," and that represented by the arrow pointing toward the left as "the reverse reaction."

Most chemical reactions are reversible. There are, however, many reactions that can hardly be thought of properly as reversible processes. It would be difficult indeed, if not impossible, to find experimental conditions that would make possible the complete reversal of the processes involved in the burning of a fuel such as coal, the decomposition of sugar by means of heat, the digestion of foodstuffs of complex composition, etc. It is wholly conceivable that all chemical changes are reversible and that the chemist's inability to bring about the reversal of some of these complex reactions is only the result of inadequate knowledge.

12.2. Rates of Reaction

The study of reversible reactions that reach a condition of equilibrium is largely concerned with the investigation of the comparative rates of two opposing reactions. With reference to chemical changes, the use of the term *rate* (or velocity, or speed) has to do with the quantity of material undergoing chemical transformation in unit time. The production of crude petroleum is expressed in terms of barrels per day. In an entirely analogous manner, the chemist speaks of the decomposition of potassium chlorate as proceeding at a rate of 0.1 g. per sec., or 1 mole per hr., etc.

12.3. Approach to a Condition of Dynamic Equilibrium

Before proceeding to any detailed study of specific cases, it is helpful to attempt to visualize the sequence of events leading to the establishment of a state of dynamic equilibrium. This may be done in a general way without reference to any particular reaction, and the resulting mental picture is equally applicable to both physical and chemical equilibria.

Suppose that two substances, A and B, react to form two other substances, C and D, and that the reaction is reversible.

$$A + B \rightleftharpoons C + D$$

If 1 mole of A and 1 mole of B are brought together, the forward reaction is the only one that can occur initially because some of C and D must be formed before the reverse reaction can occur at all. Initially, the rate of reaction between molecules of A and B is rapid because there are many of these molecules present and they collide (and react) frequently. However, as the available molecules of A and B are used up, the frequency of collision decreases and the rate of the forward reaction becomes slower and slower. In the meantime, the available number of molecules of C and D has been increasing steadily, and this in turn permits the rate of the reverse reaction to increase in proportion. So, while the rate of the forward reaction steadily decreases, the rate of the reverse reaction steadily increases. Finally, the rates of the two opposing reactions become equal, and the two reactions continue to occur without any further net gain in either direction. The reactions have then arrived at a condition of dynamic equilibrium.

12.4. Completion of Reactions

In their practical applications either for small-scale laboratory use or in commercial use, reactions are usually carried out for the purpose of producing some desired product or combination of products. Advantage is taken of the union of nitrogen and hydrogen in the synthesis of ammonia,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

but, as is indicated by the equation, the reaction is reversible and reaches a condition of equilibrium. In this or in any similar case, the problem faced by the chemist is that of determining how much of the desired product can be formed before equilibrium is established. In other words, it is desired to cause one reaction to proceed as nearly as possible to completion.

Reactions that otherwise would come to a state of equilibrium may be caused to go to completion by removing one of the products of the reaction. The production of iron on an industrial scale may be represented by the reversible reaction,

$$Fe_3O_4 + 4\overline{CO} \rightleftharpoons 3Fe + 4\overline{CO_2}$$

If this reaction is carried out in an apparatus of the type shown in Fig. 49, the forward reaction may be caused to go to completion. The CO_2

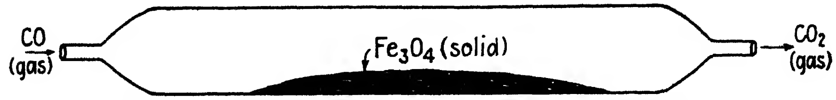


FIG. 49.—Conditions leading to completion of the reaction:

$$Fe_3O_4 + 4\overline{CO} \rightarrow 3Fe + 4\overline{CO_2}.$$

which is formed in the forward reaction is removed and is of course unable to come into contact with the Fe and thereby participate in the reverse reaction. By this arrangement the reverse reaction is eliminated by keeping apart those reactants which are necessary for the occurrence of the reverse reaction. If, on the other hand, it was necessary for some reason to carry out this reaction in a closed vessel (Fig. 50), a state of equilibrium could not be avoided. Under these conditions, net gain in the direction of the formation of iron can be realized only until the two reactions reach equilibrium unless ways can be found to influence the rate of the forward reaction at the expense of the reverse reaction.

FIG. 50.—Conditions leading to establishment of the equilibrium:

$$Fe_3O_4 + 4\overline{CO} \rightleftharpoons 3Fe + 4\overline{CO_2}.$$

Factors That Influence Reactions in Equilibrium. Fortunately, it is possible to exercise some control over reactions in equilibrium. The two reactions involved do not always respond in the same manner to changes in experimental conditions. It is often found, for example, that the forward reaction is favored by an increase in temperature more than is the reverse reaction. This change must therefore hinder the reverse reaction. Whatever may be accomplished in terms of net gain in one direction must of necessity come at the expense of net change in the opposite direction. Because the essential problem is one of relative rates of reaction, the factors that affect sys-

tems in equilibrium are the same as have already been indicated as having a bearing upon the rates of any reactions, *viz.*, concentration, temperature, and catalysis.

12.5. Methods of Expressing Concentration

From the point of view of the kinetic-molecular theory, the occurrence of a chemical reaction depends upon collisions between molecules of the reacting substances. The *total weight* of a given reactant is therefore less important than is the *total number of available molecules.* Although it is not convenient to deal with figures representing the actual number of molecules contained in any chosen unit of volume, the same purpose is accomplished by expressing concentration in terms of gram-molecular weights (or moles) since a mole of any substance represents a definite number of molecules (6.02×10^{23} molecules).

Suppose, for example, that 22 g. of hydrogen gas are placed in a 1-liter flask and that 22 g. of oxygen are contained in another 1-liter flask. In terms of weight per unit volume, the concentrations of hydrogen and oxygen (denoted by C_{H_2} and C_{O_2}, respectively) are

$$\begin{aligned} C_{H_2} &= 22 \text{ g. per } 1000 \text{ ml.} \\ &= 0.022 \text{ g. per ml.} \\ C_{O_2} &= 22 \text{ g. per } 1000 \text{ ml.} \\ &= 0.022 \text{ g. per ml.} \end{aligned}$$

In terms of *molecular concentration*, denoted by $[H_2]$ and $[O_2]$, respectively, the concentrations of hydrogen and oxygen are

$$\begin{aligned} [H_2] &= \frac{22 \div 2.016}{1000} \\ &= 0.1091 \text{ mole per ml.} \\ [O_2] &= \frac{22 \div 32}{1000} \\ &= 0.0007 \text{ mole per ml.} \end{aligned}$$

Thus, it is apparent that the number of moles per unit of volume is markedly different in the two cases even though the weight per unit of volume is the same. Whenever concentrations are expressed by symbols or formulas enclosed by brackets, molecular concentrations are indicated. An expression such as $[H_2]$ is read "the molecular concentration of hydrogen."

Concentration of Solids. For reactions concerned only with gases, it is easy to see why it might be advantageous to speak in terms of molecular concentration. In a mixture of gases, the molecules can move about and come into contact with molecules of the other reac-

tant, *i.e.*, the molecules of a gas are all readily *available* for reaction, and the number of molecules present per unit of volume governs the probability of reaction. With solids, however, the situation is vastly different. Reaction can occur only at the surface of solids, *i.e.*, only where the molecules of the solid are exposed (available). If a solid lump of sulfur is allowed to react with oxygen gas to form sulfur dioxide,

$$\overline{O}_2 + S \rightarrow \overline{SO}_2$$

reaction can occur only on the exposed surface of the lump of solid sulfur. Initially, the sulfur is present at a definite concentration expressed either as grams per unit of volume or gram atoms per unit of volume. As the reaction proceeds, the size of the lump of sulfur decreases; both the total weight of sulfur and the total volume occupied by solid sulfur diminish, but *the quantity of sulfur per unit of volume remains the same.* For this reason, the concentration of a solid substance may be said to remain constant.

12.6. Law of Mass Action

The manner in which the rates of reactions are influenced by concentration is described by the law of mass action, which may be stated as follows: **The rate of a chemical reaction is directly proportional to the molecular concentration of each of the reactants.** Consider the reaction,

$$\overline{H}_2 + \overline{Cl}_2 \rightleftharpoons 2\overline{HCl}$$

If 500 molecules of hydrogen and 500 molecules of chlorine are brought together at a suitable temperature in a closed container, the formation of HCl will occur and an equilibrium will be established. At equilibrium, the $[H_2]$ and $[Cl_2]$ will have definite values in moles per liter. If now the $[H_2]$ is increased by placing in the flask an additional 100 molecules of H_2, the chance that any given chlorine molecule will collide with a hydrogen molecule will certainly be enhanced. As a result of this change (increase) in the molecular concentration of hydrogen, more HCl will be formed, less Cl_2 will be present, and in time a new equilibrium will become established. At this new set of equilibrium conditions, however, more HCl will have been produced than was formed at the time the original equilibrium was established. Thus, it may be said that by increasing the molecular concentration of one of the reactants, the original equilibrium mixture was replaced by a new equilibrium mixture containing more hydrogen chloride and less chlorine. Similarly, by decreasing the molecular concentration of either of the reactants, the original equilibrium mixture could have been

replaced by one containing less hydrogen chloride. If one wished to produce HCl commercially by this reaction and if H_2 were cheap and Cl_2 expensive, it certainly would be profitable to use an excess of H_2 in order to get the maximum possible quantity of HCl from a given quantity of Cl_2.

12.7. Influence of Pressure upon Equilibria Involving Gases

An increase in the pressure exerted upon a confined gas causes the molecules to occupy a smaller total volume and hence is equivalent to an increase in molecular concentration (*i.e.*, more molecules per unit volume). Aside from this effect, another factor that must also be considered is the volume relationships between the gases which react and those which are formed in the reaction. In the synthesis of ammonia from nitrogen and hydrogen,

$$\begin{array}{ccccc} \overline{N}_2 & + & 3\overline{H}_2 & \rightleftharpoons & 2\overline{NH}_3 \\ 1 \text{ vol.} & + & 3 \text{ vol.} & = & 2 \text{ vol.} \end{array}$$

it is seen that the nitrogen and hydrogen together occupy a total of four volumes when uncombined, but occupy only two volumes when combined in the form of ammonia. If the four volumes of nitrogen and hydrogen are subjected to an increase in pressure, the gases must occupy a smaller volume. By combining to form ammonia, the two gases are responding chemically to produce the natural physical result of compression, *viz.*, a smaller total volume. Thus, the equilibrium mixture now contains more ammonia (and less hydrogen and nitrogen) owing to the increase in pressure, a fact that is utilized to advantage in the commercial production of ammonia by this reaction.

12.8. Influence of Temperature upon Reactions in Equilibrium

If one of two reactions in equilibrium is exothermal, the other must be endothermal to the same extent. Again using the synthesis of ammonia as an example,

$$\overline{N}_2 + 3\overline{H}_2 \rightleftharpoons 2\overline{NH}_3 + 24{,}500 \text{ cal.}$$

the forward reaction is seen to be exothermal. As a result, the formation of NH_3 may be made more complete by removing the heat (one of the products of the forward reaction) produced. If heat is supplied from the outside, the reverse reaction is favored since it is the one in which heat is absorbed. To obtain the best yield of ammonia, this reaction should therefore be carried out at a suitably low temperature. The manner in which a given system in equilibrium will respond to a change in temperature cannot be predicted without some knowledge of the particular reactions involved. Once this information has been

obtained by experiment, the temperature can be adjusted so that the response will result in an equilibrium mixture of the desired composition.

12.9. Influence of Catalysts upon Reactions in Equilibrium

A catalyst can influence an equilibrium only in the sense that the catalyst may increase the speed at which equilibrium may be attained, or permit an equilibrium to be established at a lower temperature without decreasing the rate. Considerable saving may be realized by causing equilibrium to become established more quickly and at a lower temperature than would be possible in the absence of a catalyst. Not only does this permit the production of a given product in shorter time, but it also reduces operating expenses because of the lesser heat energy expended.

12.10. Le Châtelier's Law

The preceding discussion has shown how systems in equilibrium respond to changes in experimental conditions. A general statement concerning the character of these responses is known as Le Châtelier's law (or principle). **If a system in equilibrium is subjected to any stress or constraint, the system will respond in such manner as will counteract the effects produced by the applied stress.** Changes in temperature, concentration, and pressure, all may be considered as constituting "stresses" or "constraints" in the sense that they tend to disturb the established conditions peculiar to a particular equilibrium.

12.11. Equilibrium Constant

When a reversible reaction is carried out for the purpose of producing a certain product for sale, the success or failure of the venture depends upon the efficiency with which the given reactants can be converted to the desired product or products. It is important, therefore, to have some means of determining experimentally just how closely a reaction approaches completion before equilibrium is established. Consider again the following reaction:

$$Fe_3O_4 + \overline{4H_2} \rightleftharpoons 3Fe + \overline{4H_2O}$$

Let R_A represent the rate of the forward reaction and R_B the rate of the reverse reaction. By the law of mass action, the rate of each reaction is proportional[1] to the molecular concentration of each of the reactants,

[1] The fact that the rate of reaction is proportional to the *product* of the molecular concentrations is related to the *probability* of collisions between molecules. If dice are being cast and only aces (single dots) are desired, the chance of turning

hence,

$$\begin{aligned} R_A &= k_1 \times [Fe_3O_4] \times [H_2] \times [H_2] \times [H_2] \times [H_2] \\ &= k_1 \times [Fe_3O_4] \times [H_2]^4 \\ R_B &= k_2 \times [Fe] \times [Fe] \times [Fe] \times [H_2O] \times [H_2O] \times [H_2O] \times [H_2O] \\ &= k_2 \times [Fe]^3 \times [H_2O]^4 \end{aligned}$$

where k_1 and k_2 are constants (numbers) which represent the rates at which the two reactions occur when the reactants are present *at unit concentration.* Since the molecular concentration of solids may be considered constant (Sec. 12.5), the terms $[Fe_3O_4]$ and $[Fe]^3$ may be replaced by the constants C and D, respectively.

$$R_A = k_1 \times C \times [H_2]^4$$

or

$$R_A = K_1 \times [H_2]^4$$

and

$$R_B = k_2 \times D \times [H_2O]^4$$

or

$$R_B = K_2 \times [H_2O]^4$$

When equilibrium becomes established at some definite temperature and pressure, the two rates of reaction must be equal, *i.e.*,

$$R_B = R_A$$

Substituting,

$$K_2 \times [H_2O]^4 = K_1 \times [H_2]^4$$

and

$$\frac{[H_2O]^4}{[H_2]^4} = \frac{K_1}{K_2}$$

$$\sqrt[4]{\frac{[H_2O]^4}{[H_2]^4}} = \sqrt[4]{\frac{K_1}{K_2}}$$

$$\frac{[H_2O]}{[H_2]} = K_e$$

K_e is the *equilibrium constant* for this particular reaction in equilibrium under a specified set of experimental conditions.

up an ace using only one die is one in six (1/6) because the die has six different faces, only one of which has the ace on it. Likewise, the chance that another ace will turn up when a second die is cast is also 1/6. When two dice are cast, the chance that both will turn up aces *simultaneously* is only 1 in 36, or $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$. This must be true because with two dice there are 36 possible face combinations, in which the ace-ace combination appears only once. With regard to chemical reactions, the same line of reasoning applies since the occurrence of a reaction depends upon the probability that the reacting molecules will appear simultaneously in a given location in space.

Meaning of the Equilibrium Constant. The equilibrium constant is a *number* which represents the ratio of the molecular concentration of H_2O and the molecular concentration of H_2 present when this particular equilibrium becomes established. The numerical value of this ratio is entirely independent of the original concentrations of the reactants, but it does change with alterations in experimental conditions such as temperature. For this particular reaction at 900°C., $K_e = 0.69$; at 1025°, $K_e = 0.78$; and at 1150°C., $K_e = 0.86$. Increase in the numerical value of K_e means that $[H_2O]$ has increased and $[H_2]$ has decreased with increase in temperature. In other words, increase in temperature produces an equilibrium mixture containing more H_2O (and, therefore, Fe, as well), which is the desired result. The larger the value of the equilibrium constant, the more nearly complete is the forward reaction; by the same token a small numerical value of K_e indicates that the forward reaction did not proceed very far before equilibrium was established.

Use of Equilibrium Constants. In actual practice it is not necessary to go through all the various steps used in deriving the equilibrium constant for the reversible reaction between iron oxide and hydrogen. The K_e for any reaction is equal to the product of the molecular concentrations of the products (each raised to the power indicated by its coefficient in the chemical equation) divided by the product of the molecular concentrations of the reactants (also raised to the indicated powers). Thus, for the reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\frac{[NH_3]^2}{[N_2] \times [H_2]^3} = K_e$$

If equilibrium has been established under a definite temperature and pressure, the extent to which the forward reaction proceeded toward completion before equilibrium was reached can be determined readily in terms of the size of the number which is the K_e. If one measures by experiment the concentration of any one of the three gases present in the mixture at equilibrium, the molecular concentration of each of the three gases can then be calculated from the chemical equation. By substituting these concentration data in the expression that is set equal to K_e and solving, the result is the numerical value of K_e. Suppose that, having done this, the value of K_e is small, thus indicating that the forward reaction has not proceeded so far toward completion as desired. The next step would be to change the experimental conditions (temperature, pressure, or concentration—or any combination thereof) and permit the establishment of a new equilibrium. From

the new value of K_e, the result of the change in conditions can be evaluated. Thus, the equilibrium constant provides a convenient means of following the course of a reaction in equilibrium as it responds to changes in conditions.

EXERCISES

1. What is the difference between physical and chemical equilibria?

2. What advantage is involved in expressing concentration in terms of molecular concentration?

3. Each of the following cases involves a certain weight of material contained in a specified volume. In each case, calculate the molecular concentration in terms of moles per liter.

   (*a*) 87.45 g. of sulfur dioxide (SO_2) gas in a volume of 1 liter.
   (*b*) 0.0862 g. of carbon monoxide (CO) gas in a volume of 1.36 cc.
   (*c*) 19.92 g. of methane (CH_4) gas in a volume of 6.19 liters.

4. State the following laws: (a) Le Châtelier's law, (*b*) the law of mass action.

5. List the experimental factors that influence reactions *in equilibrium* and give one example of the operation of each of these factors.

6. Using the method outlined in Sec. 12.11, derive the expression for the equilibrium constant for each of the following equilibria:

   (*a*) $2SO_{2(gas)} + O_{2(gas)} \rightleftharpoons 2SO_{3(gas)}$
   (*b*) $NH_{3(gas)} + HCl_{(gas)} \rightleftharpoons NH_4Cl_{(solid)}$

7. For each of the following equilibria, write the final expression representing the equilibrium constant.

   (*a*) $2NO_{(gas)} \rightleftharpoons N_2O_{4(gas)}$
   (*b*) $CaCO_{3(solid)} \rightleftharpoons CaO_{(solid)} + CO_{2(gas)}$
   (*c*) $CO_{2(gas)} + C_{(solid)} \rightleftharpoons 2CO_{(gas)}$

8. How will each of the equilibria listed in Exercises 6 and 7 be influenced by an increase in pressure?

9. In any given case, what determines the extent to which the forward reaction will have proceeded toward completion before equilibrium becomes established?

SUGGESTED READING

Journal of Chemical Education

Frost, Effect of Concentration on Reaction Rate and Equilibrium, **18,** 272 (1941).

Germann, Active and Passive Molecules and the Nature of the Mass Action Equilibrium Constant, **11,** 328 (1934).

CHAPTER XIII

CLASSIFICATION OF THE ELEMENTS

In view of the fact that at least 90 chemical elements are known to exist, one is immediately impressed by the truth that the acquisition of a detailed knowledge of the chemical and physical properties of each of these elements would be an extremely time-consuming task. Fortunately, however, it is not necessary (for most purposes) to study all the chemical elements in terms of their individual characteristics. Over a long period of time and as a composite result of the efforts of many scientists, it is possible to study the elements largely in terms of the interrelationships that they exhibit. On the other hand, one must not lose sight of the fact that, for certain purposes, each individual chemical element must be made the object of detailed study.

13.1. Historical

In the early years of the nineteenth century, chemists began to observe certain types of similarity among some of the elements known at that time. As early as 1829, Döbereiner called attention to the fact that several groups of three elements exhibited marked similarities. For example, chlorine, bromine, and iodine constitute such a "triad." Döbereiner observed that in such instances the middle element possessed properties intermediate between those of the other two elements and that the atomic weight of the middle element approximated the average of the atomic weights of the other two. Other similar triads indicated by Döbereiner include sulfur, selenium, and tellurium; calcium, strontium, and barium; phosphorus, arsenic, and antimony.

Although Döbereiner's efforts in the direction of a logical grouping of related elements represent only a meager beginning, his work undoubtedly did much to stimulate new efforts to discover relationships between the chemical elements in terms of their weights. In this connection it must be recognized that these early investigations were hampered by the facts that many of the elements were unknown, that those which were known had not been studied in sufficient detail, and that the values for the atomic weights of the then known elements were in many cases quite erroneous. Nevertheless, about 1860, the English chemist, Newlands, arranged the 14 lightest elements in *ascending* order of atomic weights and discovered that "every succeeding eighth

element is a kind of repetition of the first and that these elements stand to each other in the same relation as the extremities of one or more octaves in music." Newlands' "law of octaves" did not meet with a cordial reception on the part of his fellow chemists and became an object of ridicule. Nevertheless, some twenty years later, the Royal Society of London awarded Newlands the Davy medal for his earlier discovery.

At about the same time (1860) the French chemist, de Chancourtois, arranged the elements in a spiral line in order of increasing atomic weights and stated that the properties of the chemical elements are related to the numbers representing the atomic weights of those elements. Although all these investigators and others as well were undoubtedly contributing to progress in the desired directions, the true significance of their discoveries was not recognized for many years.

13.2. Mendelyeev Classification

The forerunner of the present classification of the elements was apparently devised entirely independently and at about the same time by the Russian, Dimitri Ivanovich Mendelyeev (Fig. 51), and the German, Lothar Meyer. About the only significant difference between the work of Meyer and that of Mendelyeev was that Meyer's studies emphasized physical properties of the elements whereas Mendelyeev's classification was made on the basis of both physical and chemical properties, with particular emphasis on the latter. Although the two investigators should share in the credit, Mendelyeev's bold and accurate prediction as to future developments caused him to become the most popular proponent of this means of classification of the elements. For example, 15 years before the element germanium (Ge) was discovered, Mendelyeev predicted that this element would be gray in color, would combine with oxygen to form a white solid oxide of the type EO_2, and that the pure element would be found to have a specific gravity of 5.5 and an atomic weight of 72. Germanium *is* a grayish-white solid having a specific gravity of 5.47, an atomic weight of 72.3, and combines with oxygen to form GeO_2 which is a white solid. As a result of these and other equally accurate predictions, the classification has come to be known as the *Mendelyeev arrangement* or classification.

As far as the 14 lightest elements are concerned, the Mendelyeev arrangement was identical with that of Newlands. However, the Mendelyeev arrangement was more inclusive than that of Newlands since the former embraced all the elements known at that time. A representation of the periodic classification as it was known in Mendelyeev's time is given in Fig. 52.

The elements were arranged by Mendelyeev in ascending order of their atomic weights. He observed that same sort of periodic recurrence of properties as was pointed out earlier by Newlands. This periodicity in chemical and physical properties may be likened to the periodic recurrence of the four seasons. Thus, each recurring summer season has detailed characteristics which are similar to (but not necessarily identical with) those of the preceding and following summer seasons. Just as two summer seasons are separated by three other and different seasons, so any two related elements are separated by a number of intervening elements.

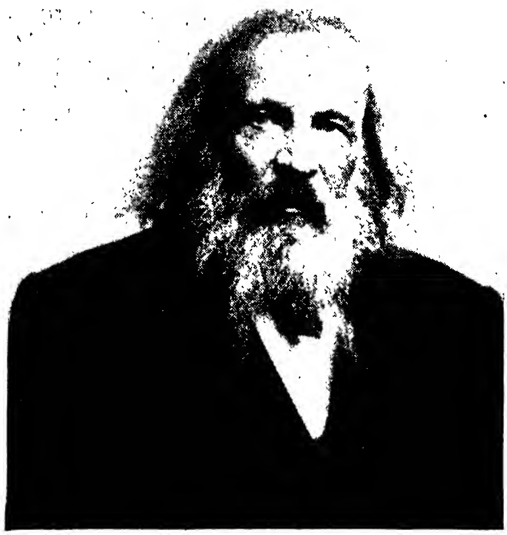


Fig. 51.—D. I. Mendelyeev (1834–1907).

Studies based upon his classification of elements led Mendelyeev to formulate what many chemists believe to be the most important generalization in the science of chemistry, *viz.*, the *periodic law*, which was stated by Mendelyeev as follows: **The properties of the elements are periodic functions of their atomic weights.** The tabular form of Mendelyeev's arrangement of the elements is known as *the periodic arrangement of the elements or the periodic table.* The modern form of the periodic table is shown in Fig. 53. As will be seen readily by comparison with Fig. 52, the original Mendelyeev arrangement has undergone many modifications, extensions, and improvements as a result of new knowledge gained since the classical work of the famous Russian scientist.

Series	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RO_2, RH_4	Group V R_2O_5, RH_3	Group VI RO_2, RH_2	Group VII R_2O_7, RH	Group VIII RO_4
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	? = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	? = 68	? = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Y = 88	Zr = 90	Nb = 94	Mo = 96	? = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	
9	—	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	

Fig. 52.—Reproduction of the essential features of Mendelyeev's original periodic table. (D. I. Mendelyeev, Die periodische Gesetzmassigkeit der chemischen Elemente, *Annalen*, Supplementband VIII, **1872,** pp. 133–229.)

Type oxide		E_2O	EO	E_2O_3	EO_2	E_2O_5	EO_3	E_2O_7	EO_4		
Type hydride		EH	EH_2	EH_3	EH_4	EH_3	EH_2	EH			
Period	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII		
1		1 H = 1.0080									
2	2 He = 4.003	3 Li = 6.940	4 Be = 9.02	5 B = 10.82	6 C = 12.010	7 N = 14.008	8 O = 16.0000	9 F = 19.00			
3	10 Ne = 20.183	11 Na = 22.997	12 Mg = 24.32	13 Al = 26.97	14 Si = 28.06	15 P = 30.98	16 S = 32.06	17 Cl = 35.457			
4	18 A = 39.944	19 K = 39.096	20 Ca = 40.08	21 Sc = 45.10	22 Ti = 47.90	23 V = 50.95	24 Cr = 52.01	25 Mn = 54.93	26 Fe = 55.85	27 Co = 58.94	28 Ni = 58.69
		29 Cu = 63.57	30 Zn = 65.38	31 Ga = 69.72	32 Ge = 72.60	33 As = 74.91	34 Se = 78.96	35 Br = 79.916			
5	36 Kr = 83.7	37 Rb = 85.48	38 Sr = 87.63	39 Y = 88.92	40 Zr = 91.22	41 Cb = 92.91	42 Mo = 95.95	43	44 Ru = 101.7	45 Rh = 102.91	46 Pd = 106.7
		47 Ag = 107.88	48 Cd = 112.41	49 In = 114.76	50 Sn = 118.70	51 Sb = 121.76	52 Te = 127.61	53 I = 126.92			
6	54 Xe = 131.3	55 Cs = 132.91	56 Ba = 137.36	*57 La = 138.92	*72 Hf = 178.6	73 Ta = 180.88	74 W = 183.92	75 Re = 186.31	76 Os = 190.2	77 Ir = 193.1	78 Pt = 195.32
		79 Au = 197.2	80 Hg = 200.61	81 Tl = 204.39	82 Pb = 207.21	83 Bi = 209.00	84 Po = ?	85			
7	86 Rn = 222	87	88 Ra = 226.05	89 Ac = ?	90 Th = 232.12	91 Pa = 231	92 U = 238.07				

* Rare earths							
	58 Ce = 140.13	59 Pr = 140.92	60 †Nd = 144.27	61	62 Sm = 150.43	63 Eu = 152	64 Gd = 156.9
	65 Tb = 159.2	66 Dy = 162.46	67 Ho = 163.5	68 Er = 167.2	69 Tm = 169.4	70 Yb = 173.04	71 Lu = 174.99

FIG. 53.—Modern Mendelyeev-type periodic table.

13.3. General Relations of the Mendelyeev Arrangement

When arranged in order of ascending atomic weights, the elements may be listed (Fig. 53) in tabular form subdivided into nine vertical columns which are known as *groups* and seven horizontal rows which are called *periods*. The detailed character of these groups and periods will be considered after some ideas concerned with the over-all relationships of the periodic table have been pointed out.

An examination of the elements listed in any given group shows that these elements exhibit certain marked similarities in properties and certain more or less regular trends in both chemical and physical characteristics. Regularities and relationships of a somewhat different character are observed when one examines the properties of the elements that fall into any given horizontal period.

Metals, Nonmetals, and Metalloids. If a diagonal line is drawn across the table, as shown in Fig. 53, and if Group VIII is neglected for the moment, the following general relations become apparent:

1. The elements tabulated below and to the left of the diagonal line are those having the properties of metals. Furthermore, for the elements in any given vertical group, the farther removed from the diagonal line the more pronounced will be the metallic character of the element. Thus the most metallic elements are listed in the lower left-hand region of the table.

2. The elements tabulated above and to the right of the diagonal line are those which, in general, do not possess any marked degree of metallic character and hence are known as the *nonmetals*. Nonmetallic character becomes more pronounced in those elements allocated to positions above and to the right of the diagonal line, with the result that the most nonmetallic elements are found in the upper right-hand region of the table.

3. If the upper right-hand region (nonmetals) and the lower left-hand region (metals) contain elements that represent the two extremes in metallic and nonmetallic character, then it follows that the diagonal line represents a line of demarkation between these two broad classes of elements. Accordingly, it is not surprising to find that the elements located on or near this line are those which are intermediate in character between the metals and the nonmetals. These elements are called *semimetals* or *metalloids*. For example, the element arsenic exhibits some properties that are characteristic of the metals and certain other properties that are most commonly possessed by nonmetals. In some of its chemical changes, arsenic acts like the metals; in other reactions its behavior is much like that of the typical nonmetals. Elements that

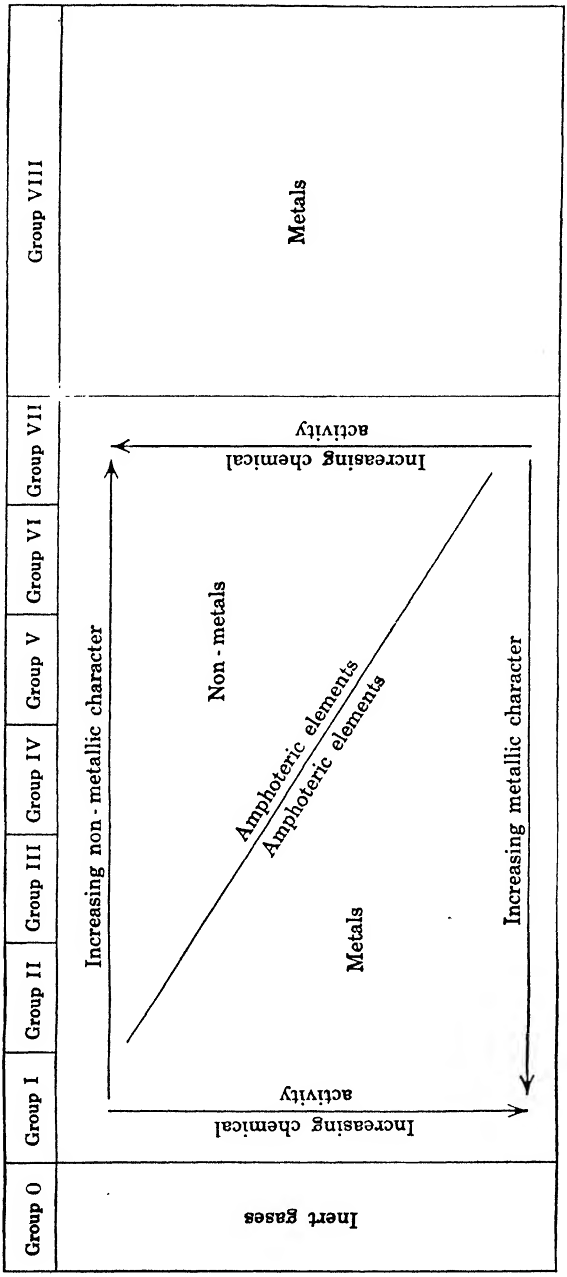


FIG. 54.—General relations in the Mendelyeev periodic table.

exhibit such dual character are sometimes said to be *amphoteric elements*.

Chemical Activity. A fairly good estimate of the relative chemical activity of an element may be gained by considering the position of that element in the periodic table. Aside from Group 0 (the elements of which do not exhibit chemical activity in the usual sense), the chemical activity among the metals *increases* with increasing atomic weight. Thus, in Group I, chemical activity increases from lithium to cesium, the latter being the most active metal known. This tendency toward increase in chemical activity with increase in atomic weight becomes less pronounced in each succeeding vertical group as one proceeds from Group I toward the center of the table.

Among the nonmetals (and excluding Group VIII) chemical activity in general *decreases* with increase in atomic weight. Accordingly, the most active nonmetals are found in the upper right-hand corner of the table. Again, this trend becomes less marked as one proceeds from Group VII toward the center of the table.

Some of these general relationships are shown diagrammatically in Fig. 54. These trends are best understood if one visualizes this diagram as being superimposed upon the periodic table (Fig. 53).

13.4. Horizontal Periods

The first "short period" begins with the inert gas, helium. The next element, lithium, is decidedly metallic in character. Beryllium, in Group II, is predominantly metallic in character although less so than lithium, but nevertheless possesses a sufficient measure of nonmetallic character to warrant its classification as a metalloid. Boron in Group III is the first element in the first short period which exhibits a predominance of nonmetallic properties. These nonmetallic characteristics are still more marked in the case of carbon in Group IV and are exhibited in increasing degree in the elements nitrogen, oxygen, and fluorine. In fact, fluorine is the most nonmetallic element known. Collectively, the elements of the first short period are frequently referred to as the *introductory elements*, since in each case a first short-period element stands at the head of each vertical group.

The first short period of eight elements is followed by a second short period (also consisting of eight elements) of which the first member is the inert gas neon. In this period, sodium is a typical metal, magnesium is somewhat less metallic than sodium, and aluminum is a typical metalloid. Nonmetallic character is first encountered in pronounced degree in the element silicon, and the remainder of the elements in this period become increasingly nonmetallic from silicon to

chlorine. It should be recognized at this point that nonmetallic character appears later in the second period than in the first. This tendency becomes more marked in each of the succeeding horizontal periods. Thus, the first predominantly nonmetallic elements in the third period are the Group V elements, vanadium and arsenic.

The third and fourth periods (long periods) consist of 18 elements each, of which 8 are "normal" elements (like those of the two first short periods) and the remaining 10 are called *transitional elements.* The fifth horizontal period consists of 8 normal elements, 10 transitional elements, and 14 "rare-earth elements," or a total of 32. Any further consideration of the character of transitional and rare-earth elements can be made best on the basis of information relating to the structures of the individual atoms (Chap. XIV). Although the long periods involve complexities that are not encountered in the two short periods, the same sorts of regularities and trends are present. Throughout each of the horizontal periods, definite gradations in both physical and chemical properties are encountered.

13.5. Vertical Groups

From the standpoint of simplification of study, a close examination of the relationships exhibited by the elements in any given group will prove to be most instructive. With exception of Groups 0 and VIII, each of the vertical groups consists of a "main family" and a subgroup. Each main family consists of normal elements, while the subgroups consist of transitional elements. The relationships between the elements of a vertical group can be appreciated best in terms of specific cases.

Group I. The main family of Group I consists of the family known as the *alkali metals*, Li, Na, K, Rb, and Cs. With increasing atomic weight, the physical properties of these decidedly metallic elements exhibit surprisingly regular trends. All these metals are solids

TABLE 14
MELTING TEMPERATURES OF THE ALKALI METALS

Alkali metal	Atomic weight	Melting temperature, °C.
Li	6.940	186
Na	22.997	97.5
K	39.096	62.3
Rb	85.44	38.5
Cs	132.91	28.5

at ordinary temperatures but are of varying hardness. Thus, lithium has the greatest hardness, sodium is next in hardness, and so on to cesium which is the softest of the alkali metals. The regularity in the trend of melting temperatures is shown by the data in Table 14, while the periodicity in atomic volumes[1] of these elements is shown in Fig. 55. The solubilities (in water) of the compounds of these elements show regular trends; in general, solubility decreases with increase in the atomic weight of the alkali metal. Thus, one would expect that RbCl would be less soluble in water than KCl, and such is the case.

Chemical properties also vary regularly throughout each main family. In Group I, chemical activity increases from lithium to cesium. If an element in a given group forms a certain type of compound, it may be anticipated that the other elements in the group will

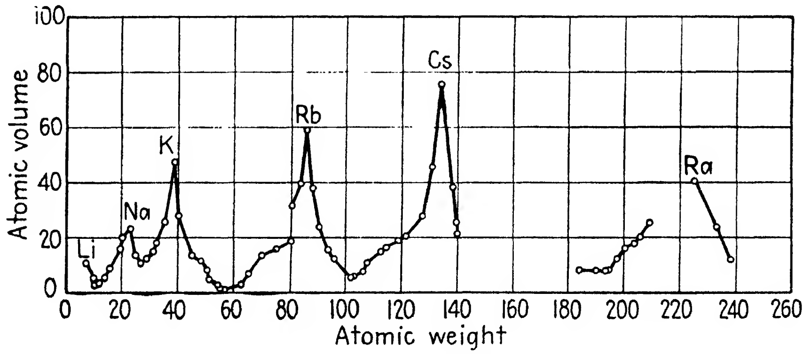


FIG. 55.—Variation in atomic volume with increasing atomic weight.

form compounds having similar properties. For example, lithium combines with oxygen to form the compound (oxide) Li_2O and with hydrogen to form the compound (hydride) LiH. Accordingly, each element in Group I may be expected to form similar compounds, and so far as the main family is concerned this has been found to be the case. To emphasize similarity in the type of compounds formed between the elements of each group and the elements oxygen and hydrogen, type formulas are given at the top of each vertical group. In these formulas, E represents any element in that group. It is not to be inferred from these type formulas that they are in any way restrictive. For example, it is not always true that all the elements in a given group will form compounds having formulas that are in accord with the type formula. Furthermore it is often true, for example, that

[1] The atomic volume of an element is the volume in cubic centimeters occupied by 1 gram-atomic weight of that element. This property is of importance since it provides an indication of relative atomic size.

a given element will form an oxide having a formula corresponding to the type formula but will also combine with oxygen to form other oxides having different formulas.

Since the metallic elements of Group I are base-forming elements, the oxides of the type E_2O dissolve in water to form bases, for example,

$$Na_2O + H_2O \rightarrow 2NaOH$$
$$Cs_2O + H_2O \rightarrow 2CsOH$$

The basic strengths of the resulting solutions increase regularly from Li to Cs; hence CsOH is a stronger base than RbOH, which in turn is a stronger base than KOH, etc.

Although the properties of the elements in the subgroup (Cu, Ag, Au) are in many respects quite different from those of the main family elements, a sufficient number of similarities are found to justify the allocation of these elements to Group I. On the other hand, the three transitional elements, Cu, Ag, and Au, show marked similarities and trends among themselves. In a later section of this chapter, further information will be provided on the subject of relationships between main families and subgroups.

Group IV. The fourth periodic group is made up of a main family consisting of C, Si, Ge, Sn, and Pb together with a subgroup containing the four transitional elements, Ti, Zr, Hf, and Th. In the main family, C and Si are nonmetallic, Ge (and to a lesser extent Sn) is a metalloid, and lead is predominantly metallic. Within the subgroup, both Ti and Zr are metalloids, while increasing degrees of metallic character are exhibited by Hf and Th. In general, the same sorts of trends in chemical and physical properties are exhibited by Group IV elements as were pointed out in connection with Group I. An important difference, however, lies in the fact that, although Group I consists entirely of metals, the entire transition from nonmetallic to metallic character is encountered in Group IV. Another important distinction lies in the fact that, in Group IV, the elements of the subgroup show many more similarities to (and fewer differences from) the elements of the main family than is the case in Group I.

Group VII. The halogen family consisting of F, Cl, Br, and I make up the main family of Group VII, while the transitional elements Mn, Ma, and Re constitute the subgroup. As is the case in Group I, the subgroup elements in Group VII exhibit surprisingly few similarities to the elements of the main family.

Perhaps in no other instance are regularities in the trends of behavior and properties illustrated better than by the halogen family.

This statement is borne out by an inspection of Table 15, in which are given certain data relating to these nonmetals.

TABLE 15
PROPERTIES OF ELEMENTS OF THE HALOGEN FAMILY

Property	F	Cl	Br	I
Physical state	Gas	Gas	Liquid	Solid
Color	Colorless	Yellow-green	Brown	Purple
Boiling temp., °C. at 1 atm.	−187°	−33.6°	61.1°	Sublimes
Heat of formation of HX*	+128,000	+44,120	+17,300	−11,820
Stability of HX*	Very stable	Stable	Fairly stable	Unstable
Solubility of HX* in 100 g. H_2O at 25°C	35.3 g.	42.0 g.	49.0 g.	57.0 g.

* Where X represents an element of the halogen family.

Within this family, metallic character increases regularly from the very nonmetallic fluorine to iodine which exhibits metallic properties in only a very limited degree. The trend in chemical activity is in the opposite direction, *i.e.*, from the *relatively* inactive iodine to the extremely active fluorine. Thus, chlorine is more active than bromine and is therefore capable of displacing bromine from its compounds. If, for example, an aqueous solution of sodium bromide is treated with gaseous chlorine, a reaction of the following type ensues:

$$2NaBr + \overline{Cl_2} \rightarrow 2NaCl + \overline{Br_2}$$

13.6. Introductory Elements

Since the elements of the first short period stand as the first elements in their respective groups, one might be led to assume that the chemical and physical characteristics of these elements might serve as a valid basis for the prediction of the properties of the other elements of each group. Such, however, is not the case. The so-called *introductory* elements exhibit many properties that are abnormal in comparison with those of the other members of their groups. For example, although each introductory element resembles the corresponding second-period element, it also usually has many properties in common with the second-period element in the next group. Thus, although Li and Na are much alike, Li also resembles Mg in many respects. Similarly, B resembles both Mg and Al, B has properties in common with both Al and Si, etc. Although these and other unusual characteristics of the introductory elements have been recognized for a long time, a simple and satisfactory explanation for this behavior is not available. Most writers seem to be content with the rather unsatis-

factory procedure of attributing the abnormal properties of the introductory elements to the relatively small size of the atoms of these elements.

Since a knowledge of the properties of *at least* two elements is necessary in order to establish the trend within a given group and since an introductory element should not be one of these, it would seem logical to choose the elements in the second and third periods. Thus, one would be led to study the elements S and Se in Group VI. If one found, for example, that Se is more metallic than S, then one would be led to predict (and correctly so) that Te should be more metallic than Se, and that O should be the least metallic element in the main family of Group VI.

13.7. Trends in the Relationship between Main Families and Subgroups

It has already been pointed out that, in Group IV, the subgroup elements show marked similarity to the elements of the main family; just the reverse is true in Groups I and VII. It should be recognized that Groups I and VII represent extreme cases in this respect and that group-subgroup similarities become more marked as one proceeds either from Group I or from Group VII toward the center of the table.

13.8. Value of the Periodic Arrangement

In view of the preceding discussion, the value of the periodic classification in the simplification of the study of the chemical elements should be so obvious as to require no further comment. In addition, the periodic arrangement serves as a basis for the prediction of hitherto unknown properties and reactions of many of the less familiar elements and in this way stimulates investigations that lead to new discoveries.

Much of the past progress in chemistry is directly attributable to the periodic classification. In Mendelyeev's time, many of the elements were unknown and the atomic weights of many of the then known elements were much in error. When, in his efforts at classification, Mendelyeev encountered difficulty, he usually attributed these difficulties to inadequate or faulty information. He left several vacancies in his table and boldly predicted that elements would be discovered later to fill in these spaces. The uncanny accuracy of his predictions has been borne out by the discovery of germanium by Winkler in 1888, of gallium by Boisbaudran in 1875, of scandium by Nilsen in 1879, etc. The arrangement aided also in the ultimate discovery of such elements as hafnium, rhenium, masurium, and the rare-earth element, illinium.

The discovery of the latter was announced in 1926 by Prof. B. S. Hopkins and his coworkers at the University of Illinois.

Mendelyeev's criticism of values for the atomic weights of certain of the elements stimulated the study and perfection of many methods for the accurate analysis of compounds of the elements. In some cases, the atomic weights were in error to an extent such that an element would appear to belong in a group not justified by the properties of the element concerned. In the majority of such cases, careful redetermination of atomic weights using improved analytical procedures resulted in the proper allocation of these elements in the table. If the periodic classification had no other value, its existence would be more than justified by the extent to which it stimulated progress in the field of analytical chemistry.

13.9. Shortcomings of the Mendelyeev Classification

The chief apparent defects in the Mendelyeev classification are that (1) the strict ascending order of atomic weights is violated in four cases, *i.e.*, argon and potassium, cobalt and nickel, tellurium and iodine, and protoactium and thorium; (2) it provides no entirely satisfactory position for the element hydrogen; (3) it provides no convenient means of tabulating the so-called *rare-earth* elements; (4) some chemically similar elements are placed in different periodic groups; and (5) some chemically dissimilar elements are allocated to the same group.

The first of these objections was eliminated by Moseley's classical work (Sec. 14.2) and the other defects listed above are, in the last analysis, not serious. It is an interesting fact that those who criticize the Mendelyeev arrangement most severely are usually those who know the least about it. It seems apropos to quote the viewpoint of the English chemist, J. Newton Friend, in this connection:

> It is not surprising that a system of classification which aims at embracing not only all of the known but also the unknown elements existing either in the free state or in various stages of combination in the universe should have its weak points. These arise from two causes, namely, an imperfect knowledge of the law itself which either leads us to seek too wide an application for it or to limit its sphere within certain narrow and arbitrary limits, and an insufficient or inaccurate knowledge of the elements it is sought to include within the scope of the law.

EXERCISES

1. Give the names of five scientists who have contributed to the development of the periodic classification and indicate briefly the nature of the contribution made by each.

2. What is the essential difference between the nature of the relationships as shown by horizontal periods and those shown by the vertical groups?

3. Into what three broad classes may all the elements be grouped and where are these classes located in relation to the periodic table?

4. Exactly what is meant when one refers to a periodic relationship?

5. In view of the positions (in the periodic table) reserved for elements 85 and 87, make predictions regarding the following properties of these elements: (*a*) atomic weight, (*b*) chemical activity, (*c*) physical state, (*d*) degree of metallic character, (*e*) chemical character of the binary hydrogen and oxygen compounds, (*f*) stability of the binary hydrogen and oxygen compounds.

6. What generalization may be made with regard to the extent to which the elements in a subgroup may be expected to resemble the elements in the main family?

7. Given the information that sulfur forms acids having the formulas H_2SO_4 and H_2SO_3, write the formulas for the acids (and for their anhydrides) which one might expect to be formed by the other elements of Group VI.

SUGGESTED READING

Journal of Chemical Education

TAYLOR, Lewis Reeve Gibbs and the Classification of the Elements, **18**, 403 (1941).

KRAUS, The Amphoteric Elements, **8**, 2126 (1931).

See references at end of Chap. XIV.

CHAPTER XIV

ATOMIC NUMBERS AND THE STRUCTURES OF ATOMS

Although the Mendelyeev classification was a major accomplishment in the direction of providing a satisfactory arrangement of the elements, the fact that it was necessary to deviate (in a few cases) from the strict ascending order of atomic weights cast doubt upon the reliability of weight alone as a sound basis for such a classification. In fact, a more fundamental basis for the classification of elements was discovered early in the present century. This more recent discovery has not led to any major alteration of the Mendelyeev arrangement but rather has confirmed and strengthened Mendelyeev's conclusions and has led to a clearer understanding of the basic principles that render possible such an orderly arrangement of the elements in conformity with their chemical and physical properties. In order to understand the full significance of these more recent developments, it is necessary to abandon the idea that an atom is the ultimate indivisible unit of matter. One must come to recognize that these atoms are composed of still smaller units of matter arranged in combinations that give rise to the atoms of the various elements.

14.1. Radioactivity

Several of the elements of high atomic weight (in periods 6 and 7 of the Mendelyeev arrangement) are unstable and undergo spontaneous disintegration. This property is known as *radioactivity* and was discovered by the French physicist, Becquerel (Fig. 56), in 1896. Although the occurrence of radioactive change or disintegration is not subject to any control by man, much can be learned through the study of this somewhat unusual behavior. The progressive disintegration of radioactive elements such as uranium, radium, or polonium, produces a variety of lighter atoms having physical and chemical properties different from those of the parent radioactive element. In addition, alpha particles, beta particles (or rays), and gamma rays are also produced. The properties of these particles or rays can be explained best in terms of an experiment illustrated by Fig. 57. If, for example, a sample of radium or a compound of radium is placed in a hole drilled into a block of lead, the particles and rays that are emitted during the

radioactive disintegration of the radium atoms may be separated (deflected) by means of a magnet arranged at right angles to the path of the emitted particles and rays. If a photographic plate is placed in the path of the particles and the rays that have been separated by use of the magnet, each kind of particle or ray will affect the photographic plate at the point of impact. The properties of each of these products of radioactive change will be considered separately.

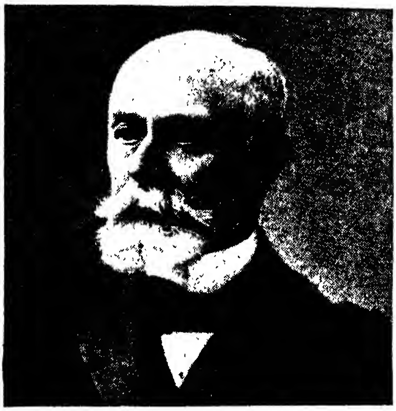


Fig. 56.—Antoine Henri Becquerel (1852–1908).

Alpha Particles. In their passage through the magnetic field, α-particles are deflected toward the negative pole of the magnet. An alpha particle has a mass almost exactly the same as the mass of a helium atom, but it differs from the neutral helium atom in that the α-particle bears two unit charges of positive electricity. Although α-particles are emitted with velocities of the order of 10,000 miles per second, they are not very penetrating since they are capable of passing through only extremely thin sheets (less than 0.1 mm. in thickness) of metals such as aluminum. α-Particles make only a relatively slight impression when they strike a photographic plate.

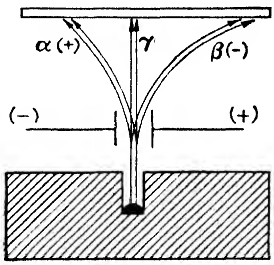


Fig. 57.—Diagram representing deflection of alpha and beta particles by a magnetic field.

Beta Particles. As shown by Fig. 57, β-particles are deflected toward the positive pole of the magnet. These particles consist of unit particles of negative electricity which are known as *electrons.* The β-particle has a mass only $\frac{1}{1840}$ that of a hydrogen atom and is emitted (from the radioactive element) with a velocity of the order of 100,000 miles per second. These β-particles (or electrons) are capable of penetrating thin sheets (1 mm. in thickness) of aluminum and are thus proved to be more penetrating than α-particles.

Gamma Rays. The γ-rays are not deflected by the magnetic field, and it may therefore be concluded that they bear neither positive nor negative electrical charge and hence are said to be *electrically neutral.*

These rays are similar to ordinary light waves except that γ-rays have extremely short wave lengths (Fig. 58). γ-Rays have essentially the same characteristics as X rays which were discovered by the German physicist, Röntgen, in 1895. That certain γ-rays are extremely penetrating is shown by the fact that they may be detected (by means of a

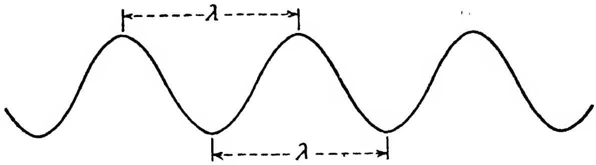


Fig. 58.—Illustration of wave length. The distance from crest to crest or from trough to trough is called one wave length and is usually designated by the Greek letter *lambda* (λ).

photographic plate) after having passed through a sheet of lead 10 in. thick.

14.2. Atomic Numbers

When an element is bombarded by a stream of electrons produced at the cathode of an X-ray tube (Fig. 59), the atoms of the element give off X rays. This procedure may be likened to the bombardment of a target by means of bullets. The element under investigation serves as the target, and the "bullets" consist of electrons impelled by

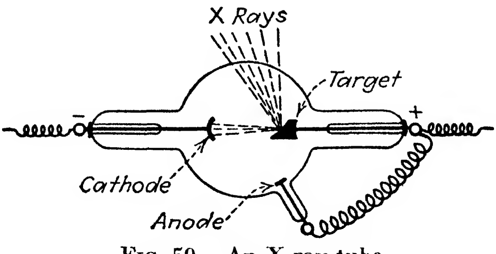


Fig. 59.—An X-ray tube.

relatively high voltages. Examination of the X-ray spectra of different elements has shown that each emits certain characteristic X radiations which are not found in the X-ray spectrum of any other element.

In 1913, the young English physicist, Moseley (Fig. 60), announced a discovery of outstanding significance. As a result of the study of the X-ray spectra of many of the elements, Moseley found that, for any two elements that stand next to each other in atomic weight, there is a constant difference between the square roots of the frequencies of vibration of the X rays characteristic of these two elements. (Frequency of vibration of X rays or light waves is the reciprocal of the

wave length and is concerned with the number of "waves" produced as the wave describes its path through a certain distance such as 1 cm. Thus, the smaller the wave length, the greater is the frequency of vibration.) If the elements are arranged in a series based upon the order indicated by the frequencies of the characteristic X rays and if each element in this series is assigned a number beginning with the number one for hydrogen (the lightest known element), these assigned numbers are related to the frequency by the expression,

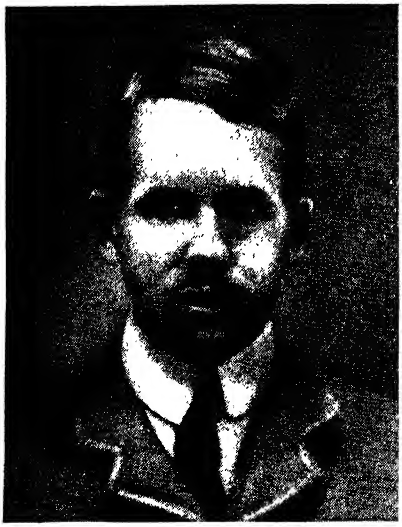


FIG. 60.—H. G. J. Moseley (1887–1915). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

$$\sqrt{f} = k(N - a)$$

where f is the frequency of vibration, N is the assigned number which is known as the *atomic number*, and k and a are constants. On this basis, the atomic number of hydrogen is 1, that of helium is 2, that of lithium is 3, etc., to the number 92 for the element uranium. The relation between frequency and atomic number is shown for a few of the elements in Fig. 61.

14.3. Atomic Numbers and the Periodic Classification

The atomic numbers are listed *above* the symbols for the elements in the periodic table shown in Fig. 53. It will be noted that, with but four exceptions, the order of atomic numbers parallels the increasing order of atomic weights and that these four exceptions are the cases in

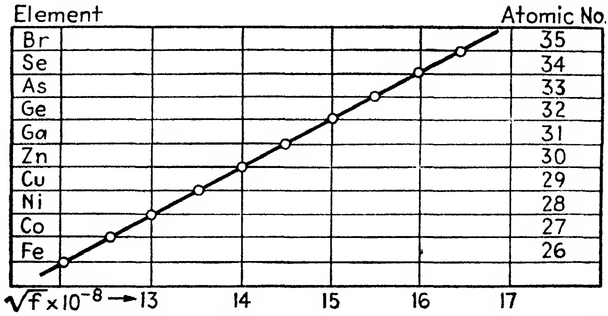


FIG. 61.—The relation between frequency and atomic number.

which Mendelyeev diverged from the ascending order of atomic weights. Thus, for reasons of known chemical behavior, Mendelyeev placed cobalt between iron and nickel (rather than following nickel) and reference to Fig. 61 will show that Moseley's work confirmed the correctness of this order. Similarly, the cases of argon and potassium, tellurium and iodine, and protoactinium and thorium are clarified when one uses atomic numbers as a criterion in place of atomic weight.

Because of the constant difference between the square roots of the frequencies of vibration of the X rays characteristic of two adjacent elements, any vacancies in the periodic table due to elements not yet discovered could be detected readily. By reference to Fig. 61, it will be seen that if the element gallium (Ga) had not yet been discovered, its existence would be indicated by a gap between Zn and Ge. During Moseley's lifetime seven such vacancies were observed, *i.e.*, there were seven atomic numbers for which no corresponding elements were known, *viz.*, numbers, 43, 61, 72, 75, 85, 87, and 91. The summary given in Table 16 represents the present status of these and four additional cases.

TABLE 16
RECENTLY DISCOVERED ELEMENTS

Atomic No.	Name	Symbol	Discoverer(s)	Date
43	Masurium*	Ma	Noddack, Tacke, and Berg	1925
61	Illinium*	Il	Hopkins	1926
72	Hafnium	Hf	Coster and von Hevesey	1923
75	Rhenium	Re	Noddak, Tacke, and Berg	1925
85	(See Sec. 16.6)			
87	(See Sec. 16.6)			
91	Protoactinium	Pa	Hahn and Meitner	1917
93	Neptunium	Np	McMillan and Abelson	1939
94	Plutonium	Pu	Seaborg, McMillan, Wahl, and Kennedy	1940
95	Americium	Am	Seaborg, James, and Morgan	1945
96	Curium	Cm	Seaborg, James, and Ghiorso	1945

* Claims to discovery not confirmed.

Restatement of the Periodic Law. In view of the developments outlined above, it becomes desirable to abandon atomic weights in favor of atomic numbers as a basis for the classification of the elements. Accordingly, the periodic law should be stated as follows: **the properties of the elements are periodic functions of their atomic numbers.** The validity of this statement will become more apparent as the student comes to recognize that the atomic numbers are related to

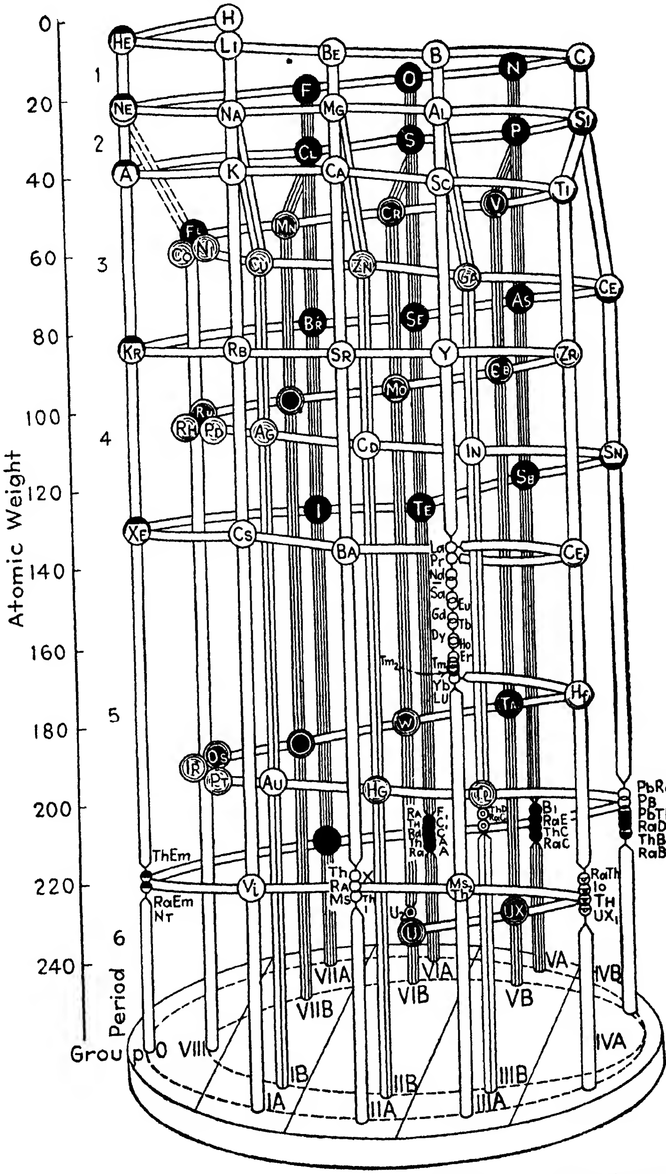


FIG. 62.—A periodic arrangement devised by Harkins and Hall [*Journal of the American Chemical Society*, **38**, 169 (1916)].

atomic structures and that atomic structures, in turn, determine the chemical and physical properties of the elements.

14.4. Modified Forms of the Periodic Arrangement

Stimulated by the success of the Mendelyeev classification, many chemists have proposed modifications designed to clarify relationships not made clear by the Mendelyeev arrangement. These tables have appeared in almost every conceivable form including numerous three-dimensional models. Examples are shown in Figs. 62 and

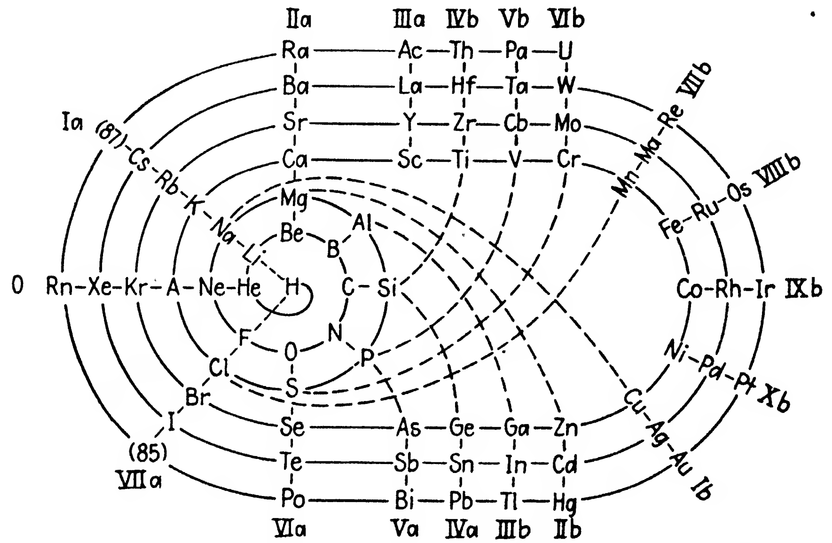


FIG. 63.—Periodic arrangement devised by Clark [*Journal of Chemical Education*, **10**, 675 (1933)]. The rare earth elements are not included.

63. Although all these efforts have served useful purposes, it is usually found that modifications designed to clarify certain relationships frequently have the disadvantage of obscuring other relationships which are portrayed adequately by the Mendelyeev table.

STRUCTURES OF ATOMS

The property of radioactivity suggests that all atoms must be made up of units of matter which are themselves even less complex than the simplest varieties of atoms. One of these particles, the electron, has already been seen to be emitted during the radioactive decay of the atoms of certain elements of high atomic weight. Two additional so-called *fundamental particles* will be considered before making any inquiry into the internal make-up of atoms and molecules.

14.5. Proton

The existence of a unit negative particle of electricity (the electron) suggested that there must be a corresponding positive unit. Experiments performed by the English physicist, Rutherford (Fig. 64), and others showed that, when certain light elements such as aluminum were bombarded by high-velocity α-particles, a new kind of particle was emitted from the atoms of the elements used as the "target." Further study demonstrated that these particles bore a positive charge and that they were lighter than α-particles. These particles were named *protons* and were found to have a mass almost identical with that of the hydrogen atom, or more precisely $^{1844}/_{1845}$ the mass of the normal hydrogen atom. The charge on the proton is equal to the charge of the electron but is opposite in sign.

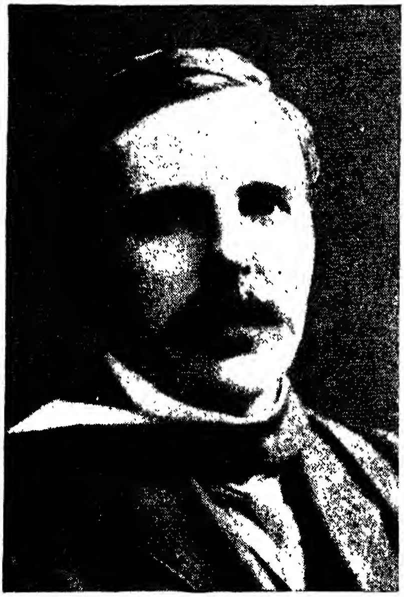


Fig. 64.—E. Rutherford (1871–1937).

14.6. Neutron

By experiments similar to those which led to the discovery of the proton, the bombardment of several elements (particularly beryllium) by α-particles was shown to result in the emission of still another particle of matter known as the *neutron*. As is suggested by its name, this particle is electrically neutral (*i.e.*, it bears neither positive nor negative charge). On the scale of atomic weights based on the assigned value of 16 for oxygen, the neutron has a mass identical with that of the hydrogen atom. The fact that the mass of the proton is $^{1844}/_{1845}$ that of the hydrogen atom plus the fact that the mass of the electron is $^{1}/_{1845}$ that of the hydrogen atom suggest that the neutron consists of one proton and one electron.

14.7. Composition of Atoms

The fact that electrons, protons, and neutrons are produced, when different atoms are subjected to conditions so extreme as to cause decomposition to occur, leads to the conclusion that these particles of matter must be present in the atoms of all the elements. Despite the

possibility that other particles (α-particles, for example) may be and probably are involved, an adequate interpretation of the structures of atoms may for present purposes be made in terms of electrons, protons, and neutrons. The properties of these fundamental particles are summarized in Table 17.

TABLE 17
COMPONENTS OF ATOMS

Particle	Charge	Mass
Neutron	0	1.008
Electron	−	$\frac{1}{1845} \times 1.008$
Proton	+	$\frac{1844}{1845} \times 1.008$

14.8. Nature of Atoms

Knowledge gained from careful experimentation extending over many years has led to certain views with regard to the nature of the atoms of the various elements. These ideas may be summarized as follows:

1. An atom of any element is an electrically neutral body containing a central *nucleus*, the dimensions of which are small in comparison with the dimensions of the atom as a whole. This nucleus consists of protons and neutrons and represents practically the entire mass (weight) of the atom. The nucleus of the atom possesses an excess of positive charges (protons), and the magnitude of this charge is identical with the *atomic number* of the element.

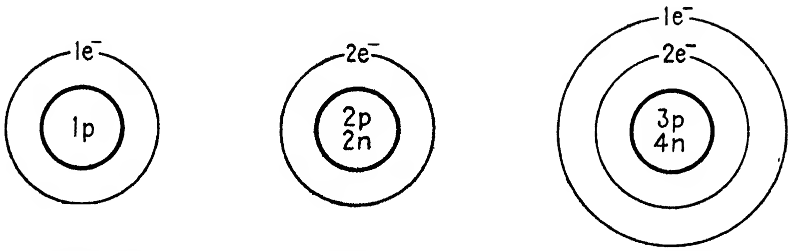
2. The extranuclear structure (*i.e.*, that outside of the nucleus) consists of electrons which may be thought of as rotating in *orbits* about the central nucleus in a manner similar to the rotation of the planets about the sun. The distance of these orbits (or *shells* as they are sometimes called) from the nucleus depends upon the complexity of the atom concerned. Since the normal atom is electrically neutral, the number of these electrons must be the same as the positive charge on the nucleus, and hence the same as the atomic number of the element concerned. The orbit or shell farthest removed from the nucleus may not contain more than 8 electrons.

Those properties of an atom which are dependent upon mass are related to the nucleus of the atom, while the chemical properties are determined by the number and arrangement of electrons outside the nucleus.

14.9. Diagrams Representing the Structures of Atoms

In terms of the foregoing ideas, it becomes desirable to attempt to represent the structures of atoms by suitable two-dimensional diagrams. Since atoms cannot be seen, it must be recognized that any static two-dimensional picture drawn to represent such dynamic three-dimensional objects may be very inaccurate. However, these diagrams are useful in the interpretation of chemical reactions and in gaining some ideas concerning the structures of molecules; hence, the use of these diagrams is justifiable.

Hydrogen Atom. The atomic number of hydrogen is 1, and the nucleus of this atom therefore must contain 1 proton which is indicated by the letter p in the small circle that represents the nucleus of the hydrogen atom (Fig. 65a). Since the atomic weight of hydrogen



(a)-Hydrogen (b)-Helium (c)-Lithium

FIG. 65.—Diagrams representing the structures of the atoms of hydrogen, helium, and lithium.

is essentially 1, this proton alone must make up the entire nucleus of the hydrogen atom. This atom is the only kind of atom containing no neutrons in the nucleus. Since the hydrogen atom is electrically neutral, the extranuclear structure must consist of 1 electron (represented by e^-), which may be pictured as rotating in an orbit outside of the nucleus. The hydrogen atom differs from all others in the simplicity of its structure. In order to gain a mental picture of the hydrogen atom, one need only visualize a single electron rotating in a circular (or elliptical) orbit around a nucleus consisting of a single proton.

Helium Atom. Since the atomic number of helium is 2, there must be 2 protons in the nucleus and 2 electrons outside of the nucleus. However, 2 protons in the nucleus are insufficient (in terms of mass) to account for the fact that the atomic weight of helium is 4. Consequently, this nucleus must contain 2 neutrons and the structure of the helium atom may be represented by the diagram of Fig. 65b, where n represents a neutron. This diagram implies that the 2 electrons rotate

in the same orbit—an implication which may be misleading. Actually, all that one wishes to represent by such a diagram is that these 2 electrons rotate in orbits that are substantially the same distance from the nucleus. Furthermore, since these electrons are in motion about the nucleus, there seems little to be gained by assigning to each a fixed position in the orbit. With but a few exceptions (Sec. 15.7) therefore it is sufficient merely to indicate the total number of electrons in the orbit, as shown in Fig. 65*b*.

Lithium Atom. That the nucleus of the lithium atom contains 3 protons follows from the atomic number of this element. However, the atomic weight of lithium is represented by the decimal fraction, 6.9. For reasons which will be given in Sec. 15.10, these fractional atomic weights may be rounded off to the nearest whole number for the purposes of the present discussion. Accordingly, the atomic weight of Li will be considered to be 7, and there must be 4 neutrons in the nucleus of the lithium atom in addition to the 3 protons. The only additional complication that arises is the fact that the orbit nearest the nucleus may not contain more than 2 electrons and, from its atomic number, the lithium atom is seen to have 3 electrons. The third electron must necessarily rotate in an orbit farther removed from the nucleus, as shown in Fig. 65*c*.

The case of lithium naturally raises the question as to the limitations on the number of electrons that may be represented as rotating in any given orbit. This information is given in Table 18 where the orbits are listed in increasing order of distance from the nucleus.

TABLE 18

MAXIMUM NUMBERS OF ELECTRONS IN THE VARIOUS ORBITS

Orbit	Number of Electrons
First	2
Second	8
Third	18*
Fourth	32
Fifth	18
Sixth	8

* It must be kept in mind that the outermost orbit may never contain more than 8 electrons. Thus, if a given atom involves only three orbits, 8 (and not 18) is the maximum number of electrons. In order for the third orbit to contain more than 8 electrons, additional orbits beyond the third are necessary.

Structures of Other Atoms. Although the preceding examples provide a basis for the representation of the structures of other atoms, any further discussion of atomic structures can be presented most profitably in relation to the periodic arrangement of the elements.

EXERCISES

1. What advantages are involved in classifying the elements in terms of atomic numbers rather than on the basis of atomic weight?

2. State the periodic law.

3. List the so-called fundamental particles of which all atoms are composed and indicate the mass and charge of each.

4. By referring only to the list of atomic weights and atomic numbers given on the inside front cover of this book (and without referring to any of the diagrams given in this or any other chapter) draw complete diagrams representing the structures of the elements having atomic numbers 1 to 20, inclusive.

5. Why is the chemist usually more interested in the extranuclear structures of the atoms than in the composition of their nuclei?

6. In terms of the structures of atoms, what is the significance of the atomic numbers?

7. Identify each of the following and describe briefly the nature and properties of each: (*a*) α-particle, (*b*) γ-ray, (*c*) β-particle.

8. If the electrons in the various orbits are subject to the attractive force of the positively charged nucleus, offer an explanation for the following facts: (*a*) In the main family of Group I, chemical activity *increases* with increase in atomic number. (*b*) In the main family of Group VII, chemical activity *decreases* with increase in atomic number.

SUGGESTED READING

Journal of Chemical Education

CONANT, Atoms, Molecules, and Ions, **5,** 25 (1928).

SHADDUCK, The Neutron, **13,** 303 (1936).

GOLDBLATT and CROUP, Essential Assumptions of a Theory of Atomic Structure, **17,** 378 (1940).

VIOL, The Commercial Production and Uses of Radium, **3,** 757 (1926).

FOSTER, Why Not Modernize the Textbook Also? I. The Periodic Table, **16,** 409 (1939).

ZMACZYNSKI, Periodic System of the Elements in a New Form, **14,** 232 (1937).

EBEL, Atomic Structure and the Periodic Table, **15,** 575 (1938).

PAYNE, A Periodic System of the Elements, **15,** 180 (1938).

IRWIN, Periodicity Patterns of the Elements, **16,** 335 (1939).

LUDER, An Improved Periodic Table, **16,** 393 (1939).

MARTIN, Another Periodic Table, **18,** 526 (1941).

LUDER, Electron Configuration as the Basis of the Periodic Table, **20,** 21 (1943).

HAZELHURST and FORNOFF, Representation of Periodic Properties of the Elements, **20,** 77 (1943).

BABOR, A Periodic Table Based on Atomic Number and Electron Configuration, **21,** 25 (1944).

EMERSON, A New Spiral Form of the Periodic Table, **21,** 111 (1944).

WAGNER and BOOTH, A New Periodic Table, **22,** 128 (1945).

Book

WEEKS, "Discovery of the Elements," Journal of Chemical Education, Easton, Pa., 1945.

CHAPTER XV

ATOMIC STRUCTURE AND THE PERIODIC TABLE

The factual information incorporated in the periodic arrangement of the elements does not, as such, offer any explanation as to why certain elements exhibit similarities in chemical and physical properties. Following the development of the periodic classification, chemists and physicists soon came to recognize that its very existence must be possible only as a result of similarities and regularities among the structures of the various kinds of atoms. It is a matter of some importance therefore to see whether the foregoing ideas concerning the structures of atoms may be correlated with, and used to explain, the relationships portrayed by the periodic table.

15.1. Structures of the Elements of the Two Short Periods

Diagrams representing the atoms of the elements of the two short periods are given in Fig. 66. An inspection of the regular addition of the electrons to the second orbit as one proceeds from Li to F and, in the second period, from Na to Cl reveals a perfect regularity in the development of these orbits. This regularity is consistent with the progressive trend from metallic to nonmetallic properties, a trend which has already been discussed.

Figure 66 also shows that in any vertical group the total number of electrons in the *outermost* orbit is the same. Thus, in Group II, Be and Mg each have 2 electrons in the outermost orbit, and this similarity in structure is responsible for the chemical similarity exhibited by these two elements. However, Be and Mg are not identical, and one would not expect them to be so for the reason that the Mg atom has, between its outermost orbit and its nucleus, a completed orbit of 8 electrons not possessed by Be. Furthermore, the nucleus of the Mg atom is heavier than that of the Be atom, and consequently a difference in physical properties is observed. If one should draw a diagram of the calcium atom (atomic number 20) this structural similarity would be seen to extend to Ca and finally to Sr, Ba, and Ra. What has been said of Group II applies also in the case of other vertical groups.

15.2. Transitional Elements

The sometimes striking lack of similarity between the elements of a main family and its subgroup has already been indicated. In Group

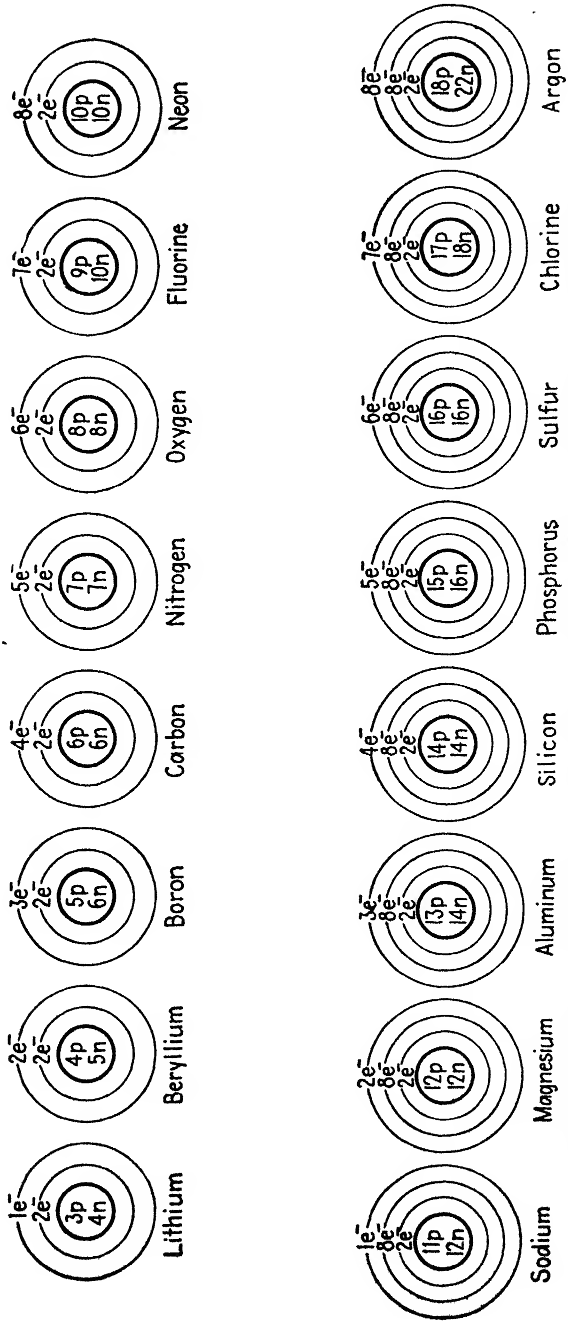


FIG. 66.—Diagrams representing the structures of the atoms of the elements of the two short periods.

Groups	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	0	Electron-shell arrangement
At. no. At. wt.	1 H 1.008																	2 He 4	2
At. no. At. wt.	3 Li 6.9	4 Be 9	5 B 10.8											6 C 12	7 N 14	8 O 16	9 F 19	10 Ne 20.2	2-8
At. no. At. wt.	11 Na 23	12 Mg 24.3	13 Al 27.1											14 Si 28	15 P 31	16 S 32	17 Cl 35.5	18 A 39.9	2-8-8
At. no. At. wt.	19 K 39.1	20 Ca 40	21 Sc 45.1	22 Ti 48.1	23 V 51	24 Cr 52	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.3	31 Ga 69.7	32 Ge 72.5	33 As 74.9	34 Se 79.2	35 Br 79.9	36 Kr 82.9	2-8-18-8
At. no. At. wt.	37 Rb 85.5	38 Sr 87.6	39 Y 88.7	40 Zr 90.6	41 Cb 93.5	42 96.0	43	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.5	53 I 126.9	54 Xe 130.2	2-8-18-18-8
At. no. At. wt.	55 Cs 132.8	56 Ba 137.4	57 La 138.9	72 Hf 178.6	73 Ta 181.5	74 W 184	75 Re 186.3	76 Os 190.9	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209	84 Po 210	85	86 Rn 222	2-8-18-32-18-8
At. no. At. wt.	87	88 Ra 226	89 Ac 226	90* Th 232.1	91 Pa 230	92 U 238.2	93 Np	94 Pu	95 Am	96 Cm									

* Presently available evidence indicates that elements 90 to 96 (inclusive) are members of a second series of rare earth elements.

Rare earth elements:	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	140.1	140.9	144.3		150.4	152	157.3	159.2	162.5	163.5	167.6	169.4	173.5	175.0

FIG. 67.—An improved form of the periodic arrangement

VI, for example, the subgroup consisting of the transitional elements Cr, Mo, W, and U show certain marked resemblances to the main family (O, S, Se, Te, and Po), and these resemblances imply that all nine of these elements must have 6 electrons in their outermost orbits. On the other hand, the differences that become apparent when one compares the properties of the subgroup elements with those of the main-family elements are the result of a property possessed by all transitional elements, *i.e.*, in the atoms of all transitional elements, the two outermost orbits are incomplete or imperfect. It is not surprising that these elements should exhibit some properties not found among elements having only one incomplete orbit.

The elements of Group VIII are also transitional elements which show trends in properties similar to the gradations found in any other group. Thus, Fe, Ru, and Os constitute a triad of structurally related atoms, consequently, they are similar in chemical and physical properties. The relationship between the Group VIII elements and the other transitional elements is shown best by a periodic table of the type given in Fig. 67.

15.3. Rare-earth Elements

In the fifth period between La (Group III, subgroup) and Hf (Group IV, subgroup), the 14 elements representing atomic numbers 58 to 71 are omitted and are listed separately at the bottom of the table (Fig. 53). These are known as the *rare-earth elements* and are most noted for their striking chemical similarity. The chemical and physical properties of these elements are so much alike that their separation from one another is an exceedingly arduous task. With only very few exceptions they exhibit a valence of three and behave in general somewhat like the other elements of the subgroup of Group III. These elements differ in structure from all other elements in that the atoms of the rare-earth elements have three incomplete or imperfect orbits.

It is an interesting and significant fact that practically all positive catalysts are found among the elements having two or more imperfect orbits, *i.e.*, the transitional or rare-earth elements or their compounds.

15.4. Structures and Properties of the Inert Gases

The preceding discussions have called attention to the existence of three classes of elements having either one, two, or three incomplete outer orbits. A fourth class consists of those elements which have no incomplete or imperfect orbits, *viz.*, the inert gases. The numbers of electrons in the orbits of these elements are given in Table 19.

TABLE 19
ARRANGEMENT OF ELECTRONS IN THE ATOMS OF THE INERT GASES

Element	Atomic number	Number of electrons in each orbit
He	2	2
Ne	10	2, 8
A	18	2, 8, 8
Kr	36	2, 8, 18, 8
Xe	54	2, 8, 18, 18, 8
Rn	86	2, 8, 18, 32, 18, 8

Comparison with Table 18 (Sec. 14.9) will show that each inert gas possesses the maximum possible number of electrons in each orbit present in the particular case.

The structures of the atoms of the inert gases are extremely stable and represent a condition that may be described as *chemical satisfaction*. These atoms have no imperfect orbits and are quite content to remain as they are. Consequently, as compared with atoms possessing one or more imperfect orbits, the inert gases exhibit little if any tendency toward participation in chemical changes. This, of course, is the reason why they are called *inert* gases.

15.5. Compound Formation

Just as the absence of uncompleted orbits results in chemical inactivity, so the presence of an orbit containing less than the maximum possible number of electrons is related to those tendencies which result in compound formation through the union of atoms of the elements. In their reactions, the atoms of the various elements tend to achieve the extranuclear structure of the nearest inert gas. The formation of compounds, therefore, may be looked upon as a manifestation of this tendency for each atom to acquire the stable arrangement and number of electrons that characterize the inert-gas structures. In the broadest sense, there are three ways in which this may be accomplished:

1. Two or more atoms may combine by a process in which one kind of atom loses certain electrons and the other kind of atom gains these electrons. This process results in the formation of what is known as an *ionic compound* (Sec. 15.6).

2. Chemical union may occur by a process in which two or more kinds of atoms share electrons, and the compounds so produced are said to be *covalent compounds* (Sec. 15.7).

3. Compounds may be formed by a combination of the *loss-gain* and *sharing* processes. That is, two or more kinds of atoms may unite

in a manner such that the chemical union is accomplished in part owing to loss and gain of electrons and in part owing to the sharing of electrons. Such compounds may be said to illustrate *intermediate types* (Sec. 15.8) since they are intermediate between the ionic and covalent types.

15.6. Ionic Compounds

The formation of an ionic compound by the loss and gain of electrons may be illustrated by the combination of lithium and fluorine. The neutral lithium atom has 1 electron in its outermost orbit and, if it could lose this 1 electron, the resulting extranuclear structure would

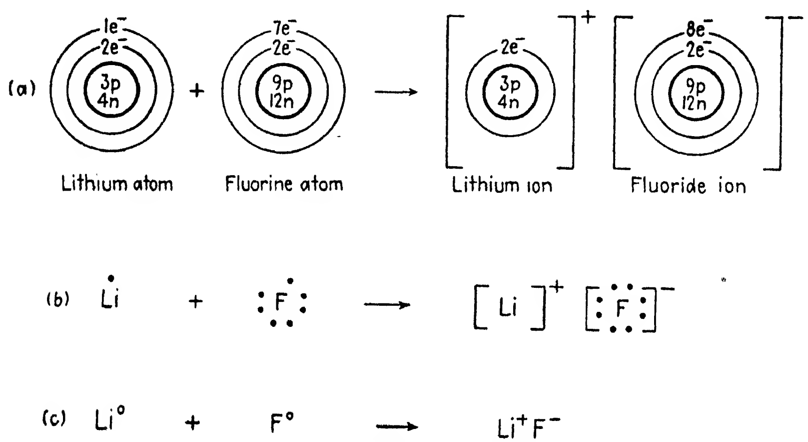


FIG. 68.—Three methods of representing the formation of lithium fluoride.

become like that of the nearest inert gas, helium. On the other hand, the neutral fluorine atom has 7 electrons in its outermost orbit and can therefore achieve an extranuclear structure like that of the inert gas, neon, provided that the fluorine atom can acquire the electron lost by the lithium atom, as shown in Fig. 68*a*. It will be observed that the only parts of these 2 atoms that appear to be involved in this chemical change are the electrons in the outermost orbits. Hence for convenience, one may equally well represent the reaction by using the symbols for the elements and surrounding these symbols by dots which represent the electrons in the outermost orbits as shown in Fig. 68*b*.

Ions. As is shown by Fig. 68*a*, the object that is formed when the neutral lithium atoms loses an electron possesses an excess of 1 proton (*i.e.*, 3 protons and 2 electrons) and hence is not an electrically neutral body. An atom (or radical) that bears an electrical charge is called an *ion*. Thus a *positive ion* is formed when a neutral lithium atom

loses an electron and a *negative ion* is formed when a neutral fluorine atom gains an electron. It follows that the combination of lithium and fluorine may be represented as shown in Fig. 68*c*, in which the zero superscripts represent the electrical neutrality (zero charge) of the original neutral atoms and in which the ions of the compound, lithium fluoride, are represented as being held together by the attraction of their unlike charges. It follows that ions must be produced when atoms lose and gain electrons; hence the name, *ionic* compounds.

Figures 68*a*, *b*, and *c* represent merely three different methods of describing the same reaction and differ only to the extent to which they provide varying degrees of complete and detailed information. To provide additional examples of the schematic representation of the

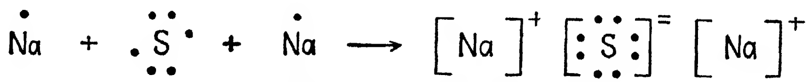


FIG. 69.—The formation of sodium sulfide.

FIG. 70.—The formation of beryllium chloride.

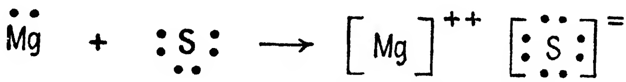


FIG. 71.—The formation of magnesium sulfide.

formation of ionic compounds, the formation of sodium sulfide, beryllium chloride, and magnesium sulfide are shown in Figs. 69, 70, and 71, respectively.

15.7. Covalent Compounds

The formation of the covalent compound, water, is represented by Fig. 72. Each hydrogen atom requires one additional electron in order to achieve a structure similar to that of helium while the oxygen atom needs two additional electrons in order to acquire an extranuclear structure like that of the neon atom. As shown in Fig. 72, these requirements are met if each hydrogen atom shares its 1 electron with oxygen while, at the same time, each hydrogen atom is permitted to share one of the electrons originally belonging to the neutral oxygen atom. This type of chemical union may be thought of as involving an "overlapping of orbits" in which the union is established by a "shared pair of electrons" (shown surrounded by dotted lines in Fig. 72) and in which this pair rotates *at the same time* in the outermost orbits of both the atoms concerned. In effect, the oxygen atom now has 8

electrons rotating in its outermost orbit while, simultaneously, 2 electrons are functioning in the orbits of each of the 2 hydrogen atoms and each kind of atom has achieved structural similarity to the nearest inert gas. Since this appears to be a situation involving no actual loss and

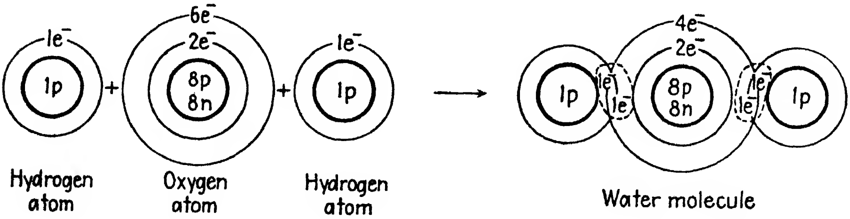


FIG. 72.—A method of representing the formation of water from hydrogen and oxygen.

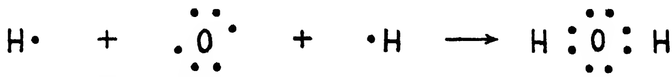


FIG. 73.—A simplified method of representing the covalent union of hydrogen and oxygen.

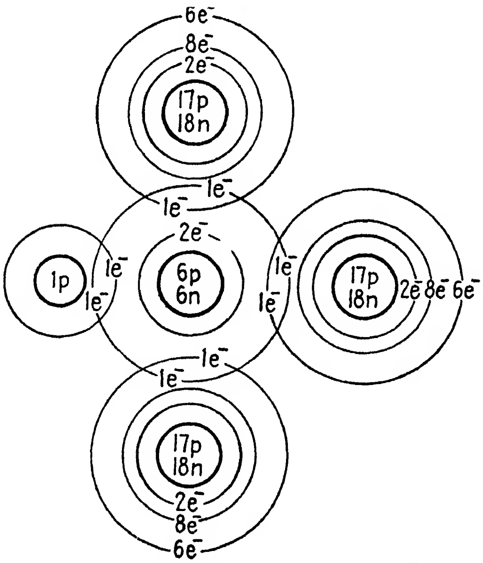


FIG. 74.—Diagram illustrating the mode of formation of the covalent compound chloroform, $CHCl_3$.

gain of electrons, it follows that ions are not formed in the process of the establishment of a true covalent combination.

Again, it is seen that only the electrons in the outermost orbits are involved; consequently, the reaction may be represented as shown in Fig. 73. Another example of a covalent combination is shown in Fig.

74, in which 1 atom of carbon is shown in combination with 1 atom of hydrogen and 3 of chlorine in the covalent compound, chloroform.

Elemental Gas Molecules. The molecules of the elemental gases have been shown to contain *at least* 2 atoms each (Sec. 7.3). In the light of the preceding ideas, the structures of these molecules may now be represented diagrammatically, as shown in Fig. 75. These cases provide additional examples of covalent combination. From these diagrams, one may also see that at least 2 and *only* 2 atoms need to be involved in each molecule. Since, upon forming a covalent union, any two such atoms possess enough electrons so that, by sharing, the requirements of each atom can be met without the involvement of a third atom. In the cases of hydrogen and chlorine, the mutual utilization of only one pair of electrons (one from each atom) is all that is necessary, while in the case of oxygen a total of 4 electrons

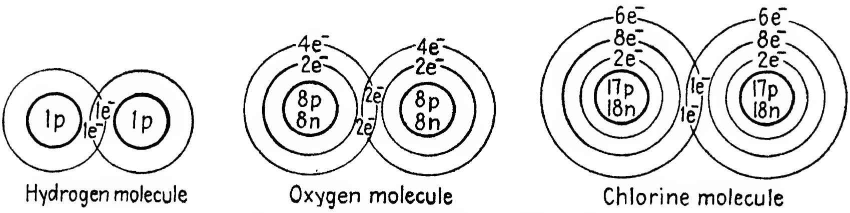


FIG. 75.—Elemental gas molecules.

(two from each atom) is required if each oxygen atom is to achieve a stable inert-gas structure. Similar diagrams may be drawn to represent the molecules of gases such as nitrogen or fluorine.

15.8. Intermediate Types

As has already been suggested in the preceding section, molecules may be formed in a manner such that both "loss-gain" and "sharing" of electrons will contribute simultaneously to the establishment of the chemical union. Thus, between the strictly ionic and the strictly covalent types of compound, there is possible a wide variety of so-called *intermediate* types. Such compounds are commonly designated in terms of the process that is involved to the greater extent. For example, if a compound is formed largely by the loss-gain process, the compound is said to be predominantly *ionic*. Similarly, predominantly covalent compounds are those in which the process of sharing of electrons plays the predominant role. Although no effort need be made to represent the structures of intermediate types, it is of importance to recognize the existence of such compounds which, after all, constitute the great majority of known inorganic chemical substances.

15.9. Valence and the Periodic Table

The relationship between the valence of an element and its position in the periodic classification may be clarified by a consideration of the following facts:

1. The number of electrons in the outermost orbit of any atom that exhibits chemical activity is the same as its vertical periodic group number (see Fig. 66).

2. Most commonly, the electrons in the outermost (or exposed) orbit are those involved in compound formation (see Figs. 68 to 74).

3. Valence has been described as a measure of *combining power* or *combining capacity*, and this power or capacity must depend upon the number of available electrons that an atom may possess in its exposed orbit.

4. Consequently, the valence of an element must be related to its position in the periodic table which in turn is dictated by the number of electrons in the outermost orbit of the atoms of that element. According to this line of reasoning, sodium should (and does) have a valence of one, aluminum should (and does) have a valence of three, etc. However, this idea cannot be pursued too far as may be shown by the following consideration of the case of sulfur.

Variable Valence. The sulfur atom (periodic Group VI) has 6 electrons in its outermost orbit and hence should be expected to exhibit a valence of six. Although sulfur does have a valence of six in many of its compounds (*e.g.*, SF_6), the valence of this element (*e.g.*, in the compound H_2S) is commonly two. Similarly, the valence of sulfur is four in the compound SO_2. Thus, it appears that the sulfur atom (and other kinds of atoms as well) can form stable compounds in which some of the electrons in the outermost orbit are not involved. The inescapable conclusion is that the valence of an element is the same as its periodic group number only when the element exhibits its maximum valence. An element, therefore, may exhibit variable valence by utilizing only a part of the electrons present in the outermost orbit of its atoms.

Among the transitional and rare-earth elements, variable valence may also appear for the reason given above and for an additional reason as well. In some cases, these elements may, in compound formation, utilize not only the electrons in the exposed orbits, but also one or more electrons from an orbit between the exposed orbit and the nucleus.

Electrovalence and Covalence. In terms of the two processes that may be concerned in the formation of compounds, it is necessary

to recognize at least two kinds of valence, *viz.*, electrovalence and covalence, which may be explained as follows:

The number of electrons lost or gained by an atom (or radical) is taken as a measure of electrovalence which is designated as positive or negative depending upon whether a positive or negative ion is formed. For example, if a calcium atom loses 2 electrons, it is said that the resulting calcium ion has a positive valence of two; and if those 2 electrons are gained by a sulfur atom, the resulting sulfur ion has a negative valence of two.

The total number of pairs of electrons shared by a given atom is a measure of the covalence of that atom. Thus, in the covalent compound SiF_4, the silicon atom has a share in four pairs of electrons and is therefore said to have a *covalence* of four. *Each* fluorine atom, however, has a share in only one pair of electrons and consequently has a covalence of one. Similarly in the water molecule (Sec. 15.7) oxygen has a covalence of two and hydrogen a covalence of one.

15.10. Isotopes

For the purpose of drawing diagrams of the atoms of the elements (Sec. 15.1) the atomic weights in certain cases were taken as the nearest whole number. It was once believed that the atomic weights of all the elements should be represented by whole numbers and that fractional atomic weights were due to errors in the determination of atomic weights by chemical methods. However, discoveries made by the English physicists, J. J. Thomson and F. W. Aston, proved that the fractional atomic weights were correct and offered a means of explaining those cases in which the atomic weights are not represented by whole numbers.

By methods that need not be described here, Thomson and Aston demonstrated that the atoms of certain elements are not all alike. For example, the atomic weight of the element nitrogen as found by the examination of ordinary nitrogen gas by chemical methods is 14.008. However, nitrogen has been shown to exist in the form of nitrogen atoms of atomic weight equal to 14 and nitrogen atoms having the weight of 15 and, in nature, the latter is present always (and only) in such quantity as to make the average atomic weight equal to 14.008. Since these two kinds of nitrogen atoms differ only with respect to weight, they differ only with regard to the number of neutrons in the nucleus. This being true, the atomic numbers and the extranuclear structures must be the same; hence the two are identical so far as their chemical properties are concerned. Atoms having the same atomic number but different atomic weights are called *isotopes*. Diagrams

of the two isotopes of nitrogen are shown in Fig. 76. From the preceding discussion, it should not be inferred that the weights of isotopes are *exactly* whole numbers. For example, the weight of chlorine 35 is actually 34.98054.

Similarly, it has been shown that most of the elements consist of mixtures of isotopes. Chlorine consists of two isotopes (Fig. 77); calcium, 4; tin, 10; etc. A complete list of known stable isotopes is given in the Appendix. Inspection of this list will reveal that, so far as is now known, only a few elements (He, Be, F, Al, P, Se, etc.) consist entirely of atoms all of which are the same. Further, it will be seen that some elements having whole-number atomic weights consist of mixtures of isotopes. For example, carbon (atomic weight = 12) consists of isotopes having weights of 12 and 13, but the quantity of the heavier isotope present is so small that its presence cannot be detected by the chemical methods used in determining the atomic weight of carbon.

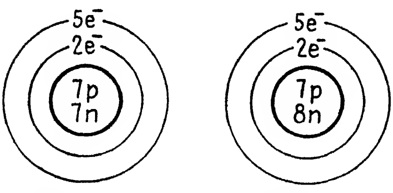


FIG. 76.—Isotopes of nitrogen.

Heavy Water In recent years, hydrogen has been shown to consist of a mixture of isotopes having masses of one, two, and three. The isotope having a mass of two has been given the name, *deuterium*. From the diagrams of Fig. 78, it will be seen that deuterium differs from ordinary hydrogen only in that the former contains 1 neutron in the nucleus and this, of course, accounts for the difference in mass.

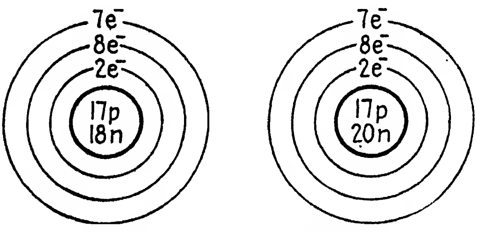


FIG. 77.—Isotopes of chlorine.

The symbol D is used to represent deuterium, and the element hydrogen is the only one for whose isotopes chemists have adopted separate names and symbols. Justification for the use of a separate symbol for deuterium can be found, perhaps, in the fact that this is truly a unique case since the two isotopes concerned exhibit a 100 per cent difference in mass.

Deuterium oxide (D_2O) represents a variety of water known as *heavy water*. As would be expected, this compound is chemically much

the same as ordinary water (H_2O) but has somewhat different physical properties. For example, D_2O boils at 101.4° and melts at 3.8°. Ordinary water contains D_2O to the extent of only 1 part in 6000. Of course, it is possible also to have a variety of water containing 1 atom of hydrogen and 1 atom of deuterium and, in view of the existence of a third isotope having a mass of 3 (this isotope has been given the name *tritium*, see Sec. 16.5), still other varieties of water may exist.

Law of Constant Composition. The existence of isotopes and the possibility of obtaining them in the pure condition may appear to challenge the validity of the law of constant composition. For example, from pure isotopes of hydrogen and chlorine, one should be able to produce several different varieties of hydrogen chloride and each would have a different percentage composition. However, each such

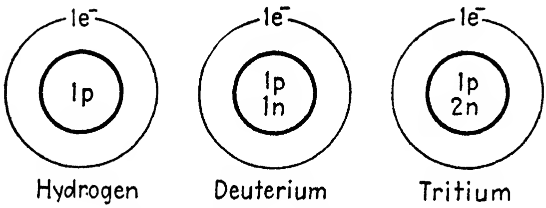


FIG. 78.—Isotopes of hydrogen.

pure compound may be considered as a separate chemical individual which, as such, conforms to the law. Furthermore, since the *average* atomic weight of each element is constant, the percentage composition of compounds will be constant except in cases such as the one cited above. Hence, it may be concluded that the existence of isotopes does not challenge the validity of the law of constant composition.

15.11. Radioactive Elements

In addition to β-rays and γ- and α-particles, the radioactive decay of radium produces isotopes of elements lighter than radium. The final product so produced is an isotope of lead having an atomic weight of 206 (as compared with the average atomic weight of ordinary lead = 207.21). Between radium and lead having an atomic weight of 206, there are produced as intermediate products, two other isotopes of lead (which are themselves radioactive) and radioactive isotopes of other heavy elements as well. Thus, it appears that radioactive decay constitutes a well-defined series of changes in which many isotopes (radioactive and otherwise) may be formed.

Radium is formed by a series which begins with the element uranium. In addition to the uranium series, there are two other series which have their beginnings in the elements thorium and actin-

ium. In the study of these more or less complex series, it is convenient to express the rates of radioactive change in terms of periods of half life. By a half-life period is meant the time required for one-half of a given weight (such as 1 g.) of an element to undergo radioactive decay. The half-life period of radium has been found to be 1590 years. The uranium series is shown in Fig. 79, which includes the half-life periods and indicates the nature of the accompanying radiations.

Definition of the Term Element. Studies that have been pursued since the term *element* was first defined (Sec. 1.5) have led to the

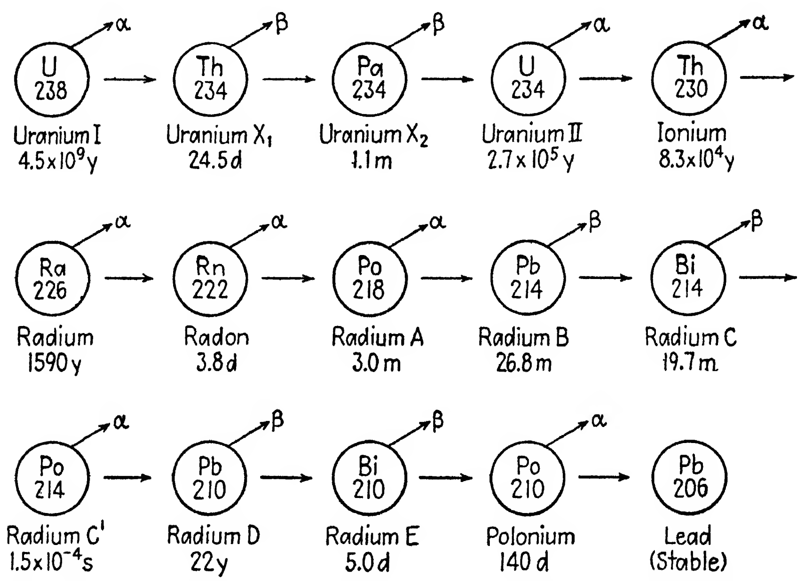


FIG. 79.—The uranium decay series. Within each circle is given the symbol of the element of which the particular series member is an isotope, together with the mass number. Below each circle is given the common name and the period of half life, where y = year, d = day, m = minute, and s = second.

conclusions that certain of the elements are unstable in the sense that they undergo spontaneous radioactive change. Furthermore, it is recognized that each element consists of atoms, all of which are not necessarily alike, and these facts suggest that the previously stated definition may be somewhat ambiguous. Since the chemical properties of an element depend upon the extranuclear structure of the atoms of the element and because the extranuclear structure is related to the atomic number, the term *element* may be defined most satisfactorily in the following manner: **An element is a substance consisting entirely of atoms having the same atomic number.** This defini-

tion is entirely satisfactory in the sense that it implies no conflict with the existence of isotopes and the facts of radioactivity.

EXERCISES

1. Into what four groups may the elements be divided in terms of the number of incomplete or imperfect electronic orbits?

2. Distinguish between the following terms: (*a*) atom and ion, (*b*) electrovalence and covalence.

3. Explain clearly how the chemical behavior of the other elements is related to the chemical inactivity of the elements of Group 0.

4. In what possible ways may atoms unite to form compounds?

5. What is the essential difference between an ionic compound and a covalent compound?

6. By means of suitable diagrams, represent the complete structure of (*a*) the ionic compound $CaCl_2$, (*b*) the covalent compound CH_4.

7. Show at least three ways of representing the formation of the ionic compound, calcium fluoride.

8. Show two different means of representing the formation of 1 molecule of nitrogen from 2 atoms of nitrogen.

9. In what two ways may certain elements exhibit variable valence?

10. Explain the meaning of the following terms: (*a*) isotope, (*b*) period of half life, (*c*) heavy water.

11. Why are the isotopes of an element not considered to be separate elements?

SUGGESTED READING

Journal of Chemical Education

SELWOOD, Heavy Water, **18**, 515 (1941).

HOPKINS, Recent Developments in the Chemistry of the Rare Earth Group, **13**, 363 (1936).

PEARCE and SELWOOD, Anomalous Valences of the Rare Earths, **13**, 224 (1936).

KING and FALL, Radioactivity and the Periodic Table, **17**, 481 (1940).

BARDWELL, Radium, **3**, 623 (1926).

CHAPTER XVI

NUCLEAR CHEMISTRY

The topics considered in the preceding two chapters have been concerned almost exclusively with the extranuclear structure of the atom. Reference has been made to the nucleus only to the extent of recognizing it as the location of the gross mass of the atom and accounting for this mass in terms of protons and neutrons when there has been occasion to represent the structures of atoms by means of diagrams.

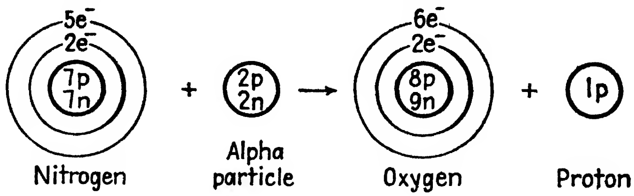
Discoveries made during the past thirty years, and more particularly during the past decade, have served to focus attention upon changes which may be brought about in the nuclei of many different kinds of atoms. These discoveries are of such far-reaching importance that they have influenced or will influence greatly practically every phase of the physical and biological sciences. Accordingly, it seems appropriate that the student should begin to become familiar with the subject of nuclear chemistry in the elementary course.

16.1. Transmutation of the Elements

For very many years, the alchemist's dream of changing base metals into gold was ridiculed even by the most reputable of scientists. Although it was known that the nuclei of certain atoms undergo alteration in the course of natural radioactive decay, man's inability to exercise any control over the nature or rate of these spontaneous decompositions probably did much to foster the belief that the nucleus of the atom was inviolate. However, in the year 1919 the English physicist, Rutherford (Fig. 64), accomplished the first transmutation of an element, and this notable discovery was quickly followed by other equally significant developments.

Using radium as a source of alpha particles, Rutherford bombarded nitrogen with these particles and converted the nitrogen to an isotope of oxygen. It will be recalled that alpha particles are helium nuclei bearing two *positive* charges and that the nucleus of the nitrogen atom bears a positive charge. However, the speed and energy of these alpha particles are such that a few of them could overcome the repulsive force of the nitrogen nuclei and thus strike these nuclei in "direct hits." The products of the interaction of nitrogen and alpha particles

proved to be oxygen atoms and protons, or in terms of a common



scheme of notation used in representing nuclear reactions,

$$_7N^{14} + {}_2\alpha^4 \longrightarrow {}_8O^{17} + {}_1p^1$$

In this equation, the subscripts represent nuclear charge and the superscripts represent the mass. As must be true in any equation, the sums of the masses and charges on the left of the arrow are equal to those on the right.

It will be noted that the transmutation of nitrogen leads to a kind of oxygen which is different from ordinary oxygen to the extent of having an additional neutron in the nucleus, hence a mass of 17 rather than the more usual 16.

As will be evident from the following paragraphs, Rutherford's accomplishment of the first transmutation led to the discovery of many similar transmutations, examples of which will be given in the following paragraphs.

16.2. Artificial Radioactivity

Fifteen years after Rutherford's transmutation of nitrogen, an equally if not more significant experiment was conducted successfully by Frederic and Irene Curie Joliot. They bombarded boron with alpha particles and produced nitrogen in a manner shown by the equation,

$$_5B^{10} + {}_2\alpha^4 \longrightarrow {}_7N^{13} + {}_0n^1$$

The remarkable feature of this transmutation was the fact that the nitrogen isotope produced was *radioactive.* These nitrogen atoms of mass 13 (rather than 14) underwent radioactive decay by emission of positive electrons, or *positrons,* to form stable carbon atoms of mass 13,

$$_7N^{13} \longrightarrow {}_6C^{13} + e^+$$

where e^+ represents the positron. For the first time, an artificial radioactive isotope had been produced, and its decay was found to occur in a manner wholly analogous to the decay of the naturally radioactive elements.

The discovery of artificial radioactivity stimulated a vast amount

of experimental work by both physicists and chemists. That this work has been productive is shown by the fact that several hundred artificially radioactive isotopes are now known, which include isotopes of practically every known element.

16.3. Methods for the Inducement of Nuclear Transformations

Both of the nuclear reactions cited above have been brought about through the use of alpha particles as the "bullets" by means of which the nuclei of nitrogen and boron atoms were bombarded. This raises the question as to whether other minute projectiles such as neutrons

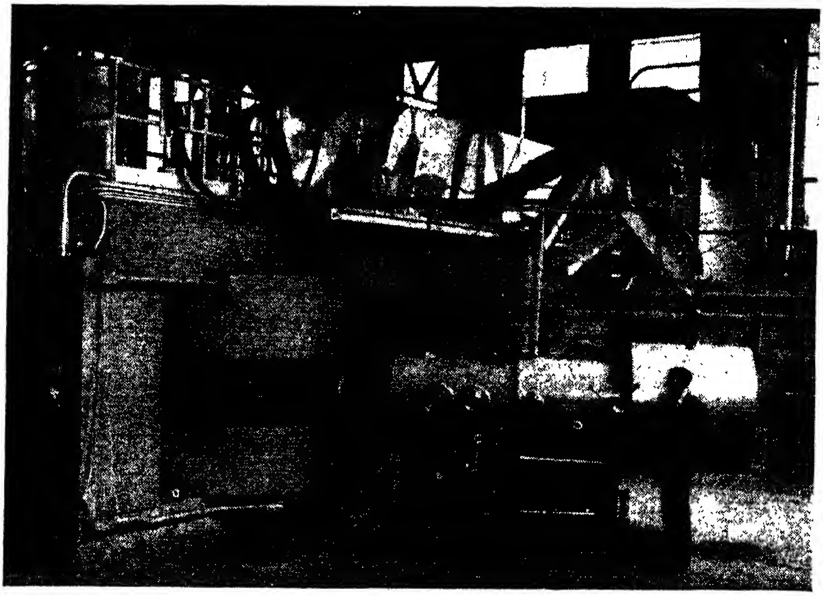


FIG. 80.—The 60-in. cyclotron located at the Radiation Laboratory, Berkeley Campus, University of California. (*Courtesy of Dr. Donald Cooksey.*)

or protons might not be used similarly to induce nuclear transformations. These and other particles have indeed been used in this manner. The nuclei of deuterium atoms are known as *deuterons* (usually represented by *d*), and these too have been used extensively. Nuclear reactions have been brought about also by the use of gamma rays.

It has already been pointed out that the bombardment of a positively charged nucleus with positive ions, such as the alpha particle, the proton, or the deuteron, suffers the disadvantage inherent in the repulsion of like charges. One means of increasing the percentage of effective "hits" is found in increasing the kinetic energy of these "ionic bullets." Of several methods of providing these high-energy

projectiles, the *cyclotron* (Fig. 80) has proved to be the most useful. This instrument was invented by E. O. Lawrence in 1932, and for this invention he was awarded the Nobel prize in 1940. The cyclotron is a device in which positive ions are accelerated in a powerful magnetic field until they attain velocities of the order of thousands of miles per second. The use of such an instrument not only makes possible the use of particles other than the alpha particles from naturally radioactive elements but also serves to increase the fraction of effective impacts between ionic bullets and nuclear "targets" that bear like charges.

Through the use of alpha particles, neutrons, etc., many nuclear reactions have been induced since Rutherford's demonstration of the first transmutation. Examples of several different types of nuclear reactions are given below, but no effort is made here to illustrate all the types that are known to occur.

An additional example of a nuclear reaction involving bombardment by means of alpha particles is found in the production of radioactive carbon of mass 14.

$$_{5}B^{11} + {}_{2}\alpha^{4} \rightarrow {}_{6}C^{14} + {}_{1}p^{1}$$

This isotope has a half life of more than 1000 years and is most likely to find widespread use in the study of carbon compounds. Other radioactive isotopes of carbon having masses of 10 and 11 have been produced but their periods of half life (8.8 sec. and 21 min., respectively) are so short as to render them relatively much less useful. Another example of the use of alpha particles to induce a nuclear reaction is the conversion of aluminum to radioactive phosphorus.

$$_{13}Al^{27} + {}_{2}\alpha^{4} \rightarrow {}_{15}P^{30} + {}_{0}n^{1}$$

Nuclear reactions induced by bombardment with protons and by deutrons are illustrated by the following examples:

$$_{6}C^{12} + {}_{1}p^{1} \rightarrow {}_{7}N^{13}$$
$$_{4}Be^{9} + {}_{1}p^{1} \rightarrow {}_{5}B^{9} + {}_{0}n^{1}$$

and

$$_{33}As^{75} + {}_{1}d^{2} \rightarrow {}_{33}As^{76} + {}_{1}p^{1}$$
$$_{10}Ne^{20} + {}_{1}d^{2} \rightarrow {}_{9}F^{18} + {}_{2}\alpha^{4}$$

Of the many known nuclear reactions induced by neutrons, the following will serve as examples of typical cases:

$$_{47}Ag^{107} + {}_{0}n^{1} \rightarrow {}_{47}Ag^{108}$$
$$_{16}S^{32} + {}_{0}n^{1} \rightarrow {}_{15}P^{32} + {}_{1}p^{1}$$
$$_{13}Al^{27} + {}_{0}n^{1} \rightarrow {}_{11}Na^{24} + {}_{2}\alpha^{4}$$
$$_{15}P^{31} + {}_{0}n^{1} \rightarrow {}_{15}P^{30} + 2{}_{0}n^{1}$$

Other examples of similar reactions will be given in the following sections.

16.4. Characteristics of Nuclear Reactions

From the foregoing discussion and illustrations, one might gain the erroneous impression that a given bombardment produces only one or two products. Such is indeed not generally true. Ordinarily, the bombardment of any given element with a particular projectile results in the occurrence of several different nuclear reactions, and it may not be possible to predict which of these competing reactions will occur to the greatest extent. Furthermore, the efficiency of utilization of the projectiles is usually extremely low; only one out of 10,000 to 1,000,000 projectiles may suffer an effective impact with a target nucleus. For these and other reasons, a given set of conditions used in a bombardment may result in only an extremely low yield of the desired product, while in other cases the yields are surprisingly high. It should be kept in mind that the science of nuclear transformations is relatively new and that many of the presently existing difficulties and uncertainties will undoubtedly be resolved by future experimental work.

The occurrence of a nuclear reaction may involve either the absorption or release of energy; hence the terms *endothermal* and *exothermal* are applicable. However, it must be recognized that there is an important difference between the energy changes involved in nuclear reactions and those in ordinary chemical changes. In relation to the masses of matter that undergo transformation, the energy changes in nuclear reactions are enormous in comparison with those which accompany ordinary chemical reactions.

It is a significant fact that the products of nuclear transformations are by no means restricted to isotopes that occur in nature. The element carbon, for example, exists in nature as a mixture of $_6C^{12}$ (98.9 per cent) and $_6C^{13}$ (1.1 per cent). The production of the artificially radioactive isotopes $_6C^{10}$, $_6C^{11}$, and $_6C^{14}$ has been mentioned previously, and these isotopes are not known to occur in nature. Although there are limitations as to the variety of isotopes of a given element which may be produced, it is evident that isotopes now known and those which will be produced in the future will become extremely useful tools in the solution of a wide variety of problems. From the standpoint of practical utilization, it is desirable to have available radioactive isotopes of appreciable half life. If one wished to conduct a prolonged chemical experiment involving a radioactive isotope having a half life of a few seconds or even a few minutes, the bulk of the original quantity of the isotope employed would have undergone radioactive

decay before the experiment could be completed. The advantages of using an isotope having a half life of hours, days, or even years are self-evident.

When the products of nuclear transformations are radioactive, they can be detected and determined quantitatively in terms of the radiations that characterize their radioactive decay. Instruments have been developed for the measurement of the quantities of radioactive isotopes present in given samples, and these methods are much more rapid and convenient than typical laborious chemical analyses.

One may rightfully raise the question as to why some products of nuclear reactions are radioactive while others are not. The answer to this question is concerned with the matter of stability of atomic nuclei. Essentially, any radioactive element whether artificial or natural is to be looked upon as abnormal. A nucleus that undergoes radioactive decay is in an unstable condition, and the process of decay always leads to stable isotopes. This tendency toward the achievement of stability is illustrated by the stepwise decay of naturally radioactive uranium to form stable isotopes of lead (Sec. 15.11) and the formation of stable carbon by the decay of artificially radioactive nitrogen (Sec. 16.2). Although the conditions resulting in the instability of atomic nuclei are fairly well understood, further consideration of these factors is beyond the scope of the present discussion.

16.5. Tritium

The existence of an isotope of hydrogen having a mass of 3 and known as *tritium* was mentioned in Sec. 15.10. This isotope is present in ordinary hydrogen but at a concentration so low that its isolation presents very great difficulties.

By means of suitable nuclear transformations, tritium has been produced under experimental conditions such that the isolation of this isotope is less difficult than its isolation from natural sources. Thus tritium (symbol, T) may be formed by bombardment of deuterium with deuterons,

$$_1D^2 + {}_1d^2 \rightarrow {}_1T^3 + {}_1p^1$$

or better, by bombardment of lithium with neutrons,

$$_3Li^6 + {}_0n^1 \rightarrow {}_1T^3 + {}_2\alpha^4$$

Tritium is also reported to be one of the products obtained by bombardment of fluorine, beryllium, antimony, copper, or silver with deuterons, or the bombardment of boron and nitrogen with neutrons.

Tritium is the simplest known radioactive isotope. It decays by

emission of beta particles to form an isotope of helium and has a half life of 31 years.

16.6. Elements 85 and 87

In Table 16 (14.3) no commitment was made with respect to the discovery of the elements of atomic numbers 85 and 87. Numerous claims have been made to the discovery of these elements in naturally occurring minerals, but most of these claims have failed of confirmation because of the use of unsound experimental methods or faulty interpretation of experimental results.

In 1940 Corson, Mackenzie, and Segrè of the University of California announced the production of a radioactive isotope of element 85 (the last member of the halogen family) by bombardment of bismuth with alpha particles.

$$_{83}\mathrm{Bi}^{209} + {}_2\alpha^4 \rightarrow {}_{85}(\quad)^{211} + 2\,{}_0n^1$$

The quantity of the isotope produced in this manner was extremely small but nevertheless sufficient to permit study of some of the chemical properties of this element and its somewhat unusual radioactive decay. Relatively recent claims to the discovery of isotopes of element 85 have been made also by Hulubei and Chauchois in 1939 and by Minder in 1940. It cannot now be stated with certainty as to who will be credited ultimately with the discovery of this element.

Hulubei in 1936 and Perey in 1937 announced the discovery of naturally radioactive isotopes of element 87, which is the last member of the family of alkali metals. It is possible that both of these claims will be confirmed and that element 87 will be isolated eventually from mineral sources. In any event, one may predict with confidence that isotopes of element 87 will be produced by nuclear transformations, if in fact such has not been done already.

16.7. Neptunium and Plutonium

In 1939, McMillan and Abelson reported the production of the first element having an atomic number greater than that of uranium (atomic number 92). By bombarding uranium with neutrons, they produced an element of atomic number 93 which later was named *neptunium* (Np). The formation of neptunium depends upon capture of a neutron by an atom of $_{92}U^{238}$ to form $_{92}U^{239}$ which decays by emission of beta particles.

$$_{92}\mathrm{U}^{238} + {}_0n^1 \rightarrow {}_{92}\mathrm{U}^{239}$$
$$_{92}\mathrm{U}^{239} \rightarrow {}_{93}\mathrm{Np}^{239} + e^-$$

McMillan and Abelson predicted that the radioactive element $_{93}Np^{239}$ would decay by emission of beta particles to form an element of atomic number 94. This prediction was soon confirmed by the work of Seaborg, McMillan, Wahl, and Kennedy who produced element 94 and made detailed studies of its chemical properties. To this new element was assigned the name *plutonium* and the symbol Pu.

$$_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + e^-$$

Further emphasis on the importance of the element plutonium will be encountered in Sec. 16.9.

16.8. Nuclear Fission

The fact that uranium is capable of undergoing a process known as *fission* was discovered as an indirect result of the use of neutrons as projectiles in the production of artificially radioactive isotopes. At the University of Rome, the Italian physicist, Fermi, bombarded many different elements with neutrons and thereby produced a considerable number of new radioactive isotopes. The use of neutrons as projectiles has the distinct advantage that the collision of these uncharged particles with nuclei is not hindered by the repulsion of like charges. Largely for this reason, the use of neutrons has been most fruitful in the inducement of nuclear transformations; in fact, helium is the only available element having stability sufficient to resist transmutation by bombardment with neutrons.

Fermi's bombardment of uranium by neutrons led to radioactive products which for a time were believed to be the then unknown elements 93 and 94 (Np and Pu). In 1939, however, the German chemists Hahn and Strassman proved that one of the products of the bombardment of uranium with neutrons is an isotope of *barium*. Since the atomic weight of uranium is nearly twice that of barium, it was immediately apparent that the uranium atoms must have undergone a process of cleavage into at least two smaller fragments. The discovery of the "splitting" or fission of uranium by Hahn and Strassman led to a vast amount of effort directed toward the identification of other "fission products" of uranium. Many have been identified and the following are cited merely as a few examples: Kr, Y, Sr, Rb, Zr, Se, La, Sn, Cb, Te, Ce, Mo, Br, etc.

It has been found that the occurrence of fission in uranium is due to the presence of $_{92}U^{235}$ which makes up only $7/10$ of 1 per cent of natural uranium. It has been learned also that other elements such as thorium, protoactinium, neptunium, and plutonium are capable of

undergoing fission and that fission may be induced not only by neutrons but also by protons, deutrons, alpha particles, and even gamma rays.

16.9. Atomic Energy

The most striking aspect of nuclear fission is the tremendous release of energy that occurs. For example, each fission in $_{92}U^{235}$ is accompanied by the liberation of energy in the amount of 200 million electron volts. To use a now familiar analogy, this means that the energy obtainable from 1 lb. of $_{92}U^{235}$ is roughly equivalent to that made available by the burning of 10,000 tons of coal. The possibility of utilizing atomic energy became apparent when it was learned that each fission of $_{92}U^{235}$ produces not only two lighter elements, but neutrons as well. Thus one fission produces neutrons which in turn may induce fission of other atoms of $_{92}U^{235}$ and thereby initiate a nuclear chain reaction which would result in the liberation of vast quantities of energy. However, predictions relative to the early utilization of atomic energy were uniformly pessimistic because of the difficulty of separating $_{92}U^{235}$ from the much more abundant $_{92}U^{238}$.

During the latter years of the Second World War, the utilization of atomic energy in the development of atomic bombs became a reality as the result of two distinct accomplishments. Although it had been predicted freely that the separation of $_{92}U^{235}$ presented almost unsurmountable difficulties, ingenious methods for the accomplishment of this separation and the production of usable quantities of this isotope were devised and put into operation at Oak Ridge, Tenn. Since isotopes are chemically identical, it was necessary to effect this separation by purely physical methods which take advantage of the very small difference in the masses of the uranium isotopes involved.

Atomic energy was made available also through the production and use of plutonium. This recently discovered element also undergoes fission with liberation of vast quantities of energy. At the Hanford Engineer Works in southeastern Washington, plutonium was formed, purified, and isolated in quantity. The reactions essential to the formation of plutonium are given below. The nature of radioactive decays are given above the arrows, and the half lives of the isotopes concerned are given below the arrows.

$$_{92}U^{238} + {_0n^1} \rightarrow {_{92}U^{239}} \xrightarrow[\text{23 min.}]{e-} {_{93}Np^{239}} \xrightarrow[\text{2.33 days}]{e-}$$

$$_{94}Pu^{239} \xrightarrow[\text{24,300 years}]{_2\alpha^4} {_{92}U^{235}}$$

These reactions are initiated by neutrons from the spontaneous fission of ${}_{92}U^{235}$. It is necessary to have present also a so-called *moderator* which may consist of hydrogen-containing substances, "heavy water," graphite, etc. The moderator must be a substance that does not capture neutrons to any appreciable extent, so that high-energy neutrons may collide with atoms of the moderator and lose energy. Some of the resulting low-energy neutrons react with ${}_{92}U^{238}$ to form plutonium as indicated above, some are lost, while others react to induce fission in other ${}_{92}U^{235}$ atoms. Thus, more neutrons are made available and a self-sustaining nuclear chain reaction is realized. The chain reaction is allowed to proceed until the concentration of plutonium becomes high enough to warrant its separation. Since plutonium is chemically different from uranium, the separation can be accomplished by chemical rather than by physical methods.

The successful utilization of atomic energy is unquestionably one of the outstanding accomplishments in the history of the physical sciences. The use of the first atomic bomb marked the beginning of a new era, and no one can foresee all the possible impacts of atomic power upon the future progress of civilization. However, it seems clear that means will be provided in the not too distant future for the use of atomic power for nonmilitary purposes.

16.10. Uses of Radioactive Isotopes

Wholly aside from the questions surrounding the utilization of atomic energy, artificially radioactive isotopes constitute a most useful tool for the study of problems in practically all branches of the physical and biological sciences. Important facts have already been brought to light through the use of radioactive isotopes of elements such as hydrogen, oxygen, sodium, iron, carbon, and phosphorus.

The use of radioactive isotopes as "tracers" is advantageous because such isotopes may be detected by virtue of the radiations that they emit. Thus, if one wished to perform an experiment employing ${}_{15}P^{32}$ which decays by emission of beta particles, one can detect the presence of a given quantity of this isotope by "counting" the number of beta particles emitted. Another advantage lies in the fact that the instruments devised for this counting of radiations are so sensitive that one usually needs to use only very small quantities of radioactive isotopes as tracers. A small amount of radioactive isotope mixed with a much larger amount of the corresponding ordinary non-radioactive element will serve to "trace" the behavior of the latter.

By such methods, for example, it has been demonstrated that phosphorus assimilated from the soil by tomato plants tends to con-

centrate in the stems and certain parts of the leaves. Similarly, radioactive zinc has been used to show that this element localizes in the seeds of tomatoes. The rate of absorption of iodine by the thyroid gland has been established by the use of $_{53}I^{128}$, and this work has done much to add to the understanding of the treatment of goiter. These and many similar uses of radioactive isotopes show that these substances are destined to be of inestimable value in the study of the mechanism of chemical reactions, problems relating to plant and animal metabolism, the diagnosis and treatment of diseases, etc.

EXERCISES

1. Define the following terms: deuteron, transmutation, fission, positron.
2. Describe briefly the contributions made by (*a*) Rutherford, (*b*) Hahn and Strassman, (*c*) Frédéric and Irene Joliot, and (*d*) Lawrence.
3. List the types of products formed upon fission of an atomic nucleus.
4. In what manner other than radioactive decay do atoms give evidence of tendencies toward achievement of stable structures?
5. How do the elements neptunium and plutonium differ from other elements?
6. Write equations which illustrate nuclear reactions induced by (*a*) neutrons, (*b*) alpha particles, (*c*) deuterons, and (*d*) protons.
7. What are the major differences between nuclear reactions and other chemical reactions?
8. What industries would most likely be influenced to the greatest extent by the industrial utilization of atomic power?
9. In what respects are nuclear reactions and other chemical reactions similar?
10. What behaviors of man-made radioactive elements are not subject to control by man?
11. What is accomplished in nuclear chemistry by the use of instruments such as the cyclotron?
12. Assuming an adequate supply of plutonium, suggest nuclear reactions which might lead to the formation of elements of atomic number greater than 94.
13. Give an example of a nuclear chain reaction.
14. Why would it be desirable to find a means of utilizing atomic energy that does not depend upon the use of uranium?

SUGGESTED READING

Journal of Chemical Education

DARROW, Nuclear Chemistry, **12,** 76 (1935).

BRESCIA and ROSENTHAL, The Production of Artificial Radio-activity, **11,** 476 (1934).

TIMM, Putting Tagged Atoms to Work, **20,** 54 (1943).

ROSENBLUM, Isotopes as Indicators, **17,** 567 (1940).

BREWER, Isotopes in the Study of Plant Growth, **18,** 217 (1941).

FOSTER, Helvetium and Moldavium, Elements 85 and 87?, **17,** 498 (1940).

FOSTER, Bombardment of Uranium with Fast and Slow Neutrons, **17,** 448 (1940).

CHAPTER XVII
IONIZATION

In connection with the study of solutions (Chap. X) some attention was devoted to the regularities in the manner in which certain physical properties of pure solvents are altered by the presence of solutes. It will be recalled, however, that this study excluded acids, bases, and salts and was restricted to solutes such as sugar and glycerol. This exclusion of certain types of solutes rather obviously suggests that their behavior must be somewhat irregular, or at least different in some respects. A limited knowledge of the various modes of compound formation (Sec. 15.5) having been acquired, it now becomes of interest to see whether the behavior of various solutes can be correlated with their classification in terms of ionic, covalent, and intermediate types. The accomplishment of this objective requires some additional information concerning the ability of substances to act as conductors (carriers) of electricity.

17.1. Conductors of Electricity

It is a familiar fact that metals such as copper, iron, silver, and zinc may be used as conductors of electricity without bringing about any change in the composition of these metals. If the properties of a copper wire are carefully examined before and after its use as a conductor, no detectable difference will be found. Metals in general, some nonmetals, and a few other substances possess the property of conduction of electricity without change in chemical composition and are known as *conductors of the first class.* The passage of electricity through a conductor of this type may be looked upon as consisting of a flow of electrons through the orbits of the atoms involved. Although the chemist frequently makes use of conductors of the first class, any detailed study of such conductors and conduction processes is perhaps more properly made in connection with courses in physics and electrical engineering.

Of greater interest to the chemist are those conductors which consist of solutions and which are known as *conductors of the second class.* These are characterized by the fact that, when they are used as carriers of electricity, changes in chemical composition always occur. Further-

more, the process by which solutions conduct electrical currents may not be likened to the "flow of electrons" suggested above, and it therefore becomes necessary to learn more about the state in which solutes exist in solutions before the distinction can be clarified.

17.2. Conduction by Solutions

If one should prepare aqueous solutions (all 0.1 molar) of a wide variety of compounds and test the ability of these solutions to act as conductors of electricity, it would be found possible to classify all of these solutions roughly into three classes: (*a*) nonconducting solutions, (*b*) weakly conducting solutions, and (*c*) strongly conducting solutions. Since the pure solvent (water) is only an exceedingly poor conductor and many pure solutes are nonconductors of electric currents, the property of conducting electricity must be peculiar to the solutions.

Since the following discussions are to be concerned with conducting solutions, those substances whose solutions are nonconductors need not be made the object of any extensive discussion. **Those substances whose solutions do not conduct electricity are known as nonelectrolytes.** Substances of this type are either entirely covalent or at least predominantly covalent in character and are illustrated by such compounds as alcohol, glycerol, and sugar. It may not be concluded, however, that all covalent compounds are nonelectrolytes.

Electrolytes. **Those substances whose solutions are conductors of electricity are called electrolytes.** Depending upon the *extent* to which their solutions act as conductors, this class of solutes may be subdivided into two groups which are known as *weak electrolytes* and *strong electrolytes.* For the purposes of the immediate discussion, acetic acid will be used as an example of a typical weak electrolyte and sodium chloride will be considered as representative of strong electrolytes.

If one should measure the electrical conductivity of a 1 M solution of $HC_2H_3O_2$ in water (*i.e.*, the extent to which the solution is capable of conducting electricity), the solution would be found to be a rather poor conductor and the magnitude of the current carried by the solution could, by means of suitable electrical instruments, be measured in amperes. Now if this same solution is diluted until it is 0.5 M with respect to $HC_2H_3O_2$, this more dilute solution will be found to be a better conductor (in relation to the total quantity of solute present) than the original 1 M solution. Progressive dilution to 0.1 M, 0.01 M, 0.001 M, etc., together with corresponding conductivity measurements will show that, with increasing dilution, the conductivity increases

until an apparent maximum is reached. Thereafter, further dilution does not result in any appreciable increase in conductivity. The results of this experiment may be represented graphically by plotting conductance against dilution as shown in Fig. 81*a*.

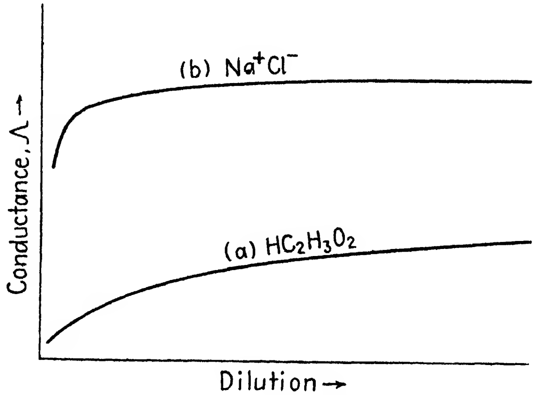


FIG. 81.—Variation in the conductance of a weak and a strong electrolyte with dilution.

A similar experiment using the strong electrolyte Na^+Cl^- as the solute would be found to lead to similar results. Of course, the conductivity will be found to be different from that of an acetic acid solution of the same concentration, but the conductivity will be found to increase with increasing dilution in much the same manner as described above. This similarity is made evident by a comparison of Fig. 81*b*, with Fig. 81*a*. The results of these two experiments would seem to require explanations to account for the fact that these solutions are conductors and for the fact that conductivity increases with dilution until a maximum conductivity is realized.

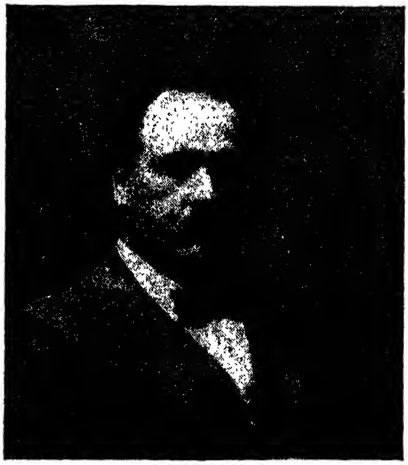


FIG. 82.—Svante Arrhenius (1859–1927).

17.3. Theory of Arrhenius

In the year 1887, the Swedish chemist, Svante Arrhenius (Fig. 82), enunciated a theory designed to explain the state in which electrolytes exist in solutions. This theory holds that whenever an acid, a base,

or a salt is dissolved in a solvent such as water, the solute *then* subdivides into smaller units which bear electrical charges. The ability of a solution of an electrolyte to act as a conductor of electricity was attributed to the presence of these charged particles, which Arrhenius called *ions* (Sec. 15.6), and to the ability of those ions to move through the solution. Also in terms of the theory of Arrhenius, the actual charge (either positive or negative) on a particular ion was believed to be equal to the valence of the atom or radical involved. Another noteworthy feature of the theory also lay in the fact that Arrhenius believed that ionization was incomplete except in extremely dilute solutions and that the actual extent to which the molecules of the solute separate into ions is dependent upon concentration.

According to the views of Arrhenius, the ionization of sodium chloride and acetic acid may be represented as follows:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$HC_2H_3O_2 \rightleftharpoons H^+ + (C_2H_3O_2)^-$$

Similarly, the ionization of other electrolytes would be represented by the equilibria,

$$Zn(NO_3)_2 \rightleftharpoons Zn^{++} + 2(NO_3)^-$$
$$CuSO_4 \rightleftharpoons Cu^{++} + (SO_4)^=$$
$$BiCl_3 \rightleftharpoons Bi^{+++} + 3Cl^-$$
$$NH_4OH \rightleftharpoons (NH_4)^+ + (OH)^-$$
$$Fe_2(SO_4)_3 \rightleftharpoons 2Fe^{+++} + 3(SO_4)^=$$

In the light of the theory of Arrhenius, it becomes possible to explain why the conductivity of a solution of an electrolyte increases with dilution and reaches a maximum value. In the case of acetic acid, for example, the ionization of increasingly dilute solutions results in increasing concentrations of ions in the equilibrium mixture. Accordingly, a concentrated solution would be expected to be a poor conductor because most of the $HC_2H_3O_2$ would be present as molecules and there would be relatively few ions present in such a solution. As this solution is made progressively more dilute, more molecules would ionize, the solution would become richer in ions and hence a better conductor. The recombination of H^+ and $(C_2H_3O_2)^-$ ions to form un-ionized molecules is, under these conditions, rendered less probable owing to the fact that in the dilute solution the ions are separated through greater distances. Finally, if the solution is made extremely (infinitely) dilute, all the molecules should separate into ions and the solution should then exhibit its maximum conductivity and further dilution should produce no further increase in conductivity. This interpretation is consistent with the experimental results described

above and shown graphically in Fig. 81. Although the theory of Arrhenius has been modified extensively since its inception, it is still useful in explaining the behavior of the great majority of the covalent compounds that behave as weak electrolytes.

In recent times, however, the Arrhenius theory has been shown to be inadequate so far as strong electrolytes (ionic compounds) and some weak electrolytes are concerned. This failure of the theory of Arrhenius may be illustrated by the case of sodium chloride. It will be recalled that sodium ions and chloride ions are formed when the ionic compound sodium chloride is formed by the process of loss and gain of electrons,

$$Na^0 + Cl^0 \rightarrow Na^+Cl^-$$

This fact has been confirmed by the examination of Na^+Cl^- crystals by means of X rays. Such studies have shown that, in the crystal, each ion occupies a fixed position in space and is surrounded by ions of opposite charge. Consequently, any given sodium ion cannot be said actually to be united with any one particular chloride ion, and this fact leads to the conclusion that discrete *molecules* of sodium chloride do not exist as such. Solid sodium chloride (and other ionic compounds as well) is to be looked upon as an electrically neutral body consisting of positive and negative ions and not involving the existence of actual unit molecules except in the sense that the crystal as a whole may be thought of as a "giant molecule."

Since ionic compounds consist of ions by virtue of their mode of formation and since the theory of Arrhenius holds that ions are formed only when the electrolyte is dissolved in a suitable solvent, some other explanation must be offered for the behavior of a strong electrolyte such as sodium chloride.

17.4. Theory of Debye and Hückel

If, in a concentrated solution, a strong electrolyte is present entirely in the form of ions, one might anticipate that such a solution would at once exhibit its maximum conductivity and that its conductivity would not be increased by dilution. That such is not the case has already been indicated (Sec. 17.2). A plausible explanation of behavior of this sort was provided by the theory of Debye and Hückel. In its most elementary aspects, this theory holds that, in a concentrated solution of a strong electrolyte, the condition of each ion is much like that which exists in the crystal. That is, each positive ion is surrounded by an "atmosphere" of negative ions (and vice versa) so that any given ion is attracted by oppositely charged ions (owing to electro-

static attraction) and is therefore retarded in its motion through the solution. This amounts to saying that, although the solute is entirely present in the form of ions, these ions are not free to move about in the solutions because of the hindering attraction of ions of the opposite charge. Thus, ions may be present in the solution without being entirely *active* as individual ions; the solute may be completely ionized but the ions are not completely disassociated from the influence of one another. Actually, one should not adopt the viewpoint that some ions are completely free or active while others are completely inactive. More properly, each ion should be thought of as exhibiting a certain *degree of activity.*

In terms of this theory, the conductivity of a solution of a strong electrolyte may be understood. The concentrated solution is a relatively poor conductor because the ions are so close together that they are unable to move readily through the solution; *i.e.*, they are greatly restricted because of the proximity of oppositely charged ions. However, as the solution is progressively diluted, the ions become separated through greater distances and are able to exhibit a greater degree of unhindered activity; hence, the conductivity increases. Finally, when the solution has been made sufficiently (infinitely) dilute, the ions are so far apart that they are relatively unaffected by the other ions and hence are able to exhibit essentially 100 per cent activity. Under these conditions, of course, the solution exhibits its maximum conductivity.

On the assumption that the theory of Debye and Hückel provides a fairly accurate picture of the condition in which strong electrolytes exist in solution, the ionization scheme

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

proposed by Arrhenius for strong electrolytes such as sodium chloride must be replaced by the equilibrium

$$Na^+Cl^- \rightleftharpoons Na^+ + Cl^-$$

A Comparison of the Two Theories. In the last analysis, there is no great difference between the theory of Arrhenius and that of Debye and Hückel. The former (1) emphasizes the formation of ions from un-ionized molecules in the solution, (2) is concerned primarily with the number of ions produced at any given concentration (*i.e.*, the *degree of ionization*) and (3) is useful in explaining the behavior of most weak electrolytes. On the other hand, the theory of Debye and Hückel (1) emphasizes both the number of and the charge on the ions, (2) is concerned largely with the freedom or activity of the ions present at any particular concentration (*i.e.*, the *degree of activity*), and (3) is

useful in interpreting the behavior of strong electrolytes including those covalent compounds which behave as strong electrolytes.

17.5. Influence of Electrolytes upon the Physical Properties of Pure Solvents

It has already been pointed out (Chap. X) that the vapor pressure, boiling temperature, and freezing temperature of a pure solvent, such as water, are changed in a *regular* fashion by the presence of nonelectrolytes such as sugar and glycerol. Electrolytes, on the other hand, produce effects that are irregular in the sense that the effects produced are in the same direction but are *excessive*. Thus, a 1 molal solution of sodium chloride actually freezes at $-3.30°C$. and not at $-1.86°$ as would be the case for a 1 molal solution of sugar. The regular lowering of the freezing temperature to the extent of $1.86°$ is characteristic of solutions of nonelectrolytes and is attributed to the presence of 6.02×10^{23} *molecules* (particles) of the solute. In the case of sodium chloride, however, the solute is present not as molecules but rather as ions which are active to only a limited degree at a concentration as high as 1 *m*. If the ions of sodium chloride were completely active in a 1 *m* solution, the number of particles (ions) would be $2 \times (6.02 \times 10^{23})$ and the freezing temperature would be $-3.72°$ $(2 \times 1.86°)$. The fact that the lowering is $3.30°$ and not $3.72°$ may be taken as indication of the degree of activity of the sodium and chloride ions in a 1 *m* solution of sodium chloride.

Similar excessive effects are produced by electrolytes upon the boiling temperatures of pure solvents, and for the same reasons. For example, the boiling temperature of a 1 *m* solution of the weak electrolyte, $HC_2H_3O_2$, is $100.522°$ and not $100.515°$ as in the case of a nonelectrolyte. The elevation of the boiling temperature is a little greater than 0.515 for the reason that a few of the original 6.02×10^{23} molecules have ionized to form H^+ and $(C_2H_3O_2)^-$ ions, thus providing a total number of particles greater than 6.02×10^{23}.

Determination of Degree of Ionization or Degree of Activity of Electrolytes. The extent to which an electrolyte at known concentration affects the boiling temperature, freezing temperature, etc., of a pure solvent may be used to determine the degree of ionization of weak electrolytes or the degree of activity of strong electrolytes. The data given in the preceding examples will serve to illustrate the method involved. In the case of the 1 *m* solution of NaCl, the lowering of the freezing temperature was found to be $3.30°$. This is $1.44°$ greater than $1.86°$ and this excess effect of $1.44°$ is a measure of the degree of activity of the ions in the 1 *m* solution. Accordingly, the degree of activity

(expressed in per cent) is given by

$$\frac{1.44}{1.86} \times 100 = 77.4 \text{ per cent activity}$$

This result, of course, should be interpreted as meaning that in a 1 *m* solution of sodium chloride, each individual ion is active (free, unhindered) only to the extent of 77.4 per cent of complete activity.

Similarly, the 1 *m* solution of the weak electrolyte, $HC_2H_3O_2$, exhibited a boiling temperature of 0.522, or 0.007° greater than the 0.515° elevation produced by an equivalent concentration of a non-electrolyte. Accordingly the degree of ionization (expressed in per cent) is

$$\frac{0.007}{0.515} \times 100 = 1.3 \text{ per cent ionization}$$

This in turn means that 1.3 per cent of the original 6.02×10^{23} molecules of $HC_2H_3O_2$ ionized to form H^+ and $(C_2H_3O_2)^-$.

17.6. Weak Electrolytes

In connection with much of the subject matter that is to follow, it is necessary for the student to acquire information concerning those common acids, bases, and salts which behave as weak electrolytes.

Acids. The common acids that behave as weak electrolytes are listed in Table 20. For those acids which contain more than one replaceable hydrogen, it is necessary to inquire as to the manner in

TABLE 20

DEGREE OF IONIZATION OF SOME WEAK ELECTROLYTES (ACIDS) IN 0.1 NORMAL SOLUTIONS AT 25°C.

Acid	Ionization process	Degree of ionization, %
Acetic	$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$	1.3
Hydrocyanic	$HCN \rightleftharpoons H^+ + CN^-$	0.002
Hydrosulfuric	$H_2S \rightleftharpoons H^+ + HS^-$	0.07
Carbonic	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	0.17
Hydrogen carbonate ion	$HCO_3^- \rightleftharpoons H^+ + CO_3^=$	0.01
Sulfurous	$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	34.0
Hydrogen sulfite ion	$HSO_3^- \rightleftharpoons H^+ + SO_3^=$	0.1
Phosphoric	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	27.0
Dihydrogen phosphate ion	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^=$	0.14
Hydrogen phosphate ion	$HPO_4^= \rightleftharpoons H^+ + PO_4^{\equiv}$	0.0002

which such acids ionize. The ionization of an acid such as carbonic acid occurs in two stages or "steps," thus,

$$H_2CO_3 \rightleftharpoons H^+ + (HCO_3)^- \qquad (1)$$

to form first a hydrogen ion and a hydrogen carbonate ion, $(HCO_3)^-$, which then participates in the second step of the ionization process,

$$(HCO_3)^- \rightleftharpoons H^+ + CO_3^= \qquad (2)$$

Similarly, the ionization of H_3PO_4 is a three-stage process involving the equilibria,

$$H_3PO_4 \rightleftharpoons H^+ + (H_2PO_4)^- \qquad (1)$$
$$(H_2PO_4)^- \rightleftharpoons H^+ + (HPO_4)^= \qquad (2)$$
$$(HPO_4)^= \rightleftharpoons H^+ + (PO_4)^{\equiv} \qquad (3)$$

Since acids that ionize in this manner are weak electrolytes, even the first step occurs to only a limited extent. Accordingly, the second step cannot occur extensively since it is limited by the extent to which $(H_2PO_4)^-$ ions, for example, are available. Since only a few of the $(H_2PO_4)^-$ ions undergo further ionization according to step (2), the third stage can be realized to only an exceedingly small extent.

Bases. The only common base that acts as a weak electrolyte is ammonium hydroxide which is formed by the reaction between gaseous ammonia and water,

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

and which ionizes according to the equilibrium,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

In 0.1 N solution at 25°, NH_4OH is ionized to the extent of only 1.3 per cent.

Salts. Although most salts are strong electrolytes, there are a few common ones whose behavior is more nearly typical of weak electrolytes. These rather exceptional cases are listed in Table 21.

TABLE 21

WEAK ELECTROLYTES (SALTS)

Name	Formula
Lead acetate	$Pb(C_2H_3O_2)_2$
Ferric thiocyanate	$Fe(CNS)_3$
Mercuric thiocyanate	$Hg(CNS)_2$
Mercuric chloride	$HgCl_2$
Mercuric cyanide	$Hg(CN)_2$
Cadmium chloride	$CdCl_2$
Cadmium bromide	$CdBr_2$
Cadmium iodide	CdI_2

Water. A very important weak electrolyte is water itself. Water molecules ionize to only an extremely slight extent under ordinary conditions. An idea as to the very small number of ions in pure water may be gained from the fact that the total weight of OH^- in 1 ton of water is 0.0017 g. More accurately, the concentration of H^+ (or OH^-) in pure water is 1×10^{-7} *N* (*i.e.*, one ten-millionth normal).

17.7. Strong Electrolytes

For the purposes of the work that is to follow, all electrolytes that have not been designated as "weak" in the preceding section are to be considered as strong electrolytes. As will be shown later (Sec. 17.8), this viewpoint is neither entirely accurate nor justifiable except on the basis of convenience.

It is not practical here to list any great number of strong electrolytes.

TABLE 22
DEGREE OF ACTIVITY OF SOME TYPICAL STRONG ELECTROLYTES IN 0.1 MOLAL SOLUTIONS AT 25°C.

Electrolyte	Degree of activity, %	Classification
Acids:		
H^+Br^-	80.2	Uni-univalent
H^+Cl^-	79.6	
$H^+(NO_3)^-$	79.0	
$H_2^+(SO_4)^=$	31.3	Uni-bivalent
Bases:		
$K^+(OH)^-$	77.2	Uni-univalent
$Na^+(OH)^-$	76.5	
$Li^+(OH)^-$	74.2	
$Ba^{++}(OH)_2^-$	....	Bi-univalent
Salts:		
Li^+Br^-	79.4	Uni-univalent
Na^+I^-	78.8	
Na^+Cl^-	77.8	
K^+Br^-	76.5	
K^+Cl^-	76.4	
$K^+(NO_3)^-$	73.2	
$Ag^+(NO_3)^-$	72.3	
$Ca^{++}Cl_2^-$	52.8	Bi-univalent and uni-bivalent
$Ba^{++}Cl_2^-$	49.5	
$Na_2^+(SO_4)^=$	43.5	
$K_2^+(SO_4)^=$	42.0	
$Mg^{++}(SO_4)^=$	16.6	Bi-bivalent
$Cd^{++}(SO_4)^=$	16.0	
$Cu^{++}(SO_4)^=$	15.8	

However, a brief list is given in Table 22, together with the degree of activity expressed in per cent, and a classification of the examples cited on the basis of the valence of the ions involved.

By inspection of the data of Table 22 it will be seen that there is a definite relationship between the degree of activity and the charge type of the ions. This is wholly in accord with the ideas embodied in the theory of Debye and Hückel. It should be rather obvious that an ion bearing two units of positive charge should be more effective in hindering the movement of a negative ion than an ion bearing only one positive charge. Similarly the $SO_4^=$ should exert a greater force of attraction toward a Na^+, for example, than would a Cl^-. It is therefore a fairly safe generalization to state that, *at equivalent concentrations, the degree of activity decreases with increase in the magnitude of the ionic charges.*

17.8. Intermediate Types

It is essential at this juncture to call attention to the fact that the foregoing classification of electrolytes into two broad classes should not be accepted without reservations. The student should keep in mind that weak electrolytes are predominantly covalent and that strong electrolytes are (with but relatively few exceptions) predominantly ionic. But, just as there are all possible gradations between covalent and ionic compounds (Sec. 15.8), so there must be a correspondingly large number of electrolytes that are intermediate between the very weak and the very strong electrolytes. In this and in other similar situations, there is some considerable merit in the practice of emphasizing the extreme types of behavior in the beginning course and deferring the study of the generally more complicated behavior of intermediate types to the more advanced courses.

17.9. Acid Salts

Since the ionization of acids containing two or more replaceable hydrogen atoms occurs in stages or steps (Sec. 17.6) and since the extent of each stage of ionization is greater than that of any subsequent step, the neutralization of such acids should also be expected to occur in a stepwise fashion. Consider, for example, the first step in the ionization of sulfurous acid,

$$H_2SO_3 \rightleftharpoons H^+ + (HSO_3)^-$$

Owing to the fact that this stage of ionization is so much more extensive than the subsequent ionization of the hydrogen sulfite ion,

$$(HSO_3)^- \rightleftharpoons H^+ + (SO_3)^=$$

it might be anticipated that the neutralization of sulfurous acid by a base such as sodium hydroxide would occur as follows:

$$H_2SO_3 + Na^+(OH)^- \rightarrow H_2O + Na^+(HSO_3)^-$$

The strong electrolyte $Na^+(HSO_3)^-$, however, consists of an anion $(HSO_3)^-$ which is a weak electrolyte but which is capable of further ionization.

$$Na^+(HSO_3)^- \rightleftharpoons Na^+ + H^+ + (SO_3)^=$$

Consequently a further reaction with a base is possible, thus,

$$Na^+(HSO_3)^- + Na^+(OH)^- \rightarrow H_2O + Na_2^+(SO_3)^=$$

The neutralization of acids containing two or more replaceable hydrogen atoms does occur in this stepwise fashion and, in the laboratory, one may neutralize such an acid either completely or partly, depending upon the quantity of base employed. The stepwise neutralization of arsenic acid will serve as a further example,

$$H_3AsO_4 + K^+(OH)^- \rightarrow H_2O + K^+(H_2AsO_4)^-$$
$$K^+(H_2AsO_4)^- + K^+(OH)^- \rightarrow H_2O + K_2^+(HAsO_4)^=$$
$$K_2^+(HAsO_4)^= + K^+(OH)^- \rightarrow H_2O + K_3^+(AsO_4)^{\equiv}$$

If a base containing more than one $(OH)^-$ is used, a similar result is obtained.

$$2H_2CO_3 + Ba^{++}(OH)_2^- \rightarrow 2H_2O + Ba^{++}(HCO_3)_2^-$$
$$Ba^{++}(HCO_3)_2^- + Ba^{++}(OH)_2^- \rightarrow 2H_2O + 2Ba^{++}(CO_3)^=$$

The preceding examples have pointed to the existence of the compounds, $Na^+(HSO_4)^-$, $K^+(H_2AsO_4)^-$, $K_2^+(HAsO_4)^=$, and $Ba^{++}(HCO_3)_2^-$. Like acids, all these compounds contain replaceable hydrogen and at the same time appear to be salts since they arise from reactions of neutralization. Compounds of this type are known as *acid salts.* These acid salts are named in different ways, two of which are illustrated in Table 23.

TABLE 23
NOMENCLATURE OF ACID SALTS

Formula	Preferred name	Alternative name
$Na^+(HSO_3)^-$	Sodium hydrogen sulfite	Sodium acid sulfite
$K^+(H_2AsO_4)^-$	Potassium dihydrogen arsenate	Primary potassium arsenate
$K_2^+(HAsO_4)^=$	Dipotassium hydrogen arsenate	Secondary potassium arsenate
$Ba^{++}(HCO_3)_2^-$	Barium hydrogen carbonate	Barium acid carbonate
$Na^+(HCO_3)^-$	Sodium hydrogen carbonate*	Sodium acid carbonate

* The common name for this compound is "sodium bicarbonate." However, in systematic nomenclature the prefix *bi-* should be avoided in naming acid salts.

Normal Salts. Salts such as $Na_2^+(SO_3)^=$, $K_3^+(AsO_4)^{\equiv}$, and $Ba^{++}(CO_3)^=$, which represent the products obtained by complete neutralization, are called *normal salts* and are assigned names in accordance with the rules of nomenclature previously discussed (Sec. 11.8).

Basic Salts. By analogy to acid salts, the existence of *basic salts* would certainly appear as a logical possibility and many salts of this type are well known. However, a consideration of their mode of formation and properties will be deferred to a later chapter.

EXERCISES

1. Distinguish clearly between the following: (*a*) conductors of the first class and conductors of the second class, (*b*) electrolytes and nonelectrolytes, (*c*) strong electrolytes and weak electrolytes, (*d*) atoms and ions, (*e*) degree of ionization and degree of activity, (*f*) acid salts and normal salts.

2. In what way are weak electrolytes, strong electrolytes, and intermediate types related to their mode of formation?

3. What facts contributed to the partial failure of the theory of Arrhenius and gave rise to the theory of Debye and Hückel?

4. Criticize the following statement: "In a solution of a strong electrolyte which exhibits 70 per cent activity, 70 out of each 100 ions are active while the remaining 30 are inactive."

5. Give a brief comparison of the theories of Arrhenius and of Debye and Hückel.

6. A 1 *m* water solution of a strong electrolyte of the type M^+X^- was found by experiment to boil at 100.887°. Calculate the degree of activity.

7. A 1 *m* water solution of a weak electrolyte of the type M^+X^- was found by experiment to freeze at −1.89° C. Calculate the degree of ionization.

8. Write systematic names for the following acid salts: $Na^+(HS)^-$, $Li^+(HSO_4)^-$, $Ca^{++}(H_2PO_4)_2^-$, $K_2^+(HPO_3)^=$.

9. What is the maximum number of acid salts that might be produced from each of the following acids: (*a*) H_2SiO_3, (*b*) H_2ZnO_2, (*c*) HNO_2, (*d*) H_3AlO_3, (*e*) H_4ZrO_4, (*f*) H_2Se, (*g*) $HAsO_3$, (*h*) H_3PO_4?

10. Where such ionization is possible, write equations (equilibria) showing the stepwise ionization of each of the acids listed in Exercise 9.

11. If only about 1 per cent of the NH_4OH molecules in a 1 *m* solution of this base is ionized, how may one account for the fact that *all* of the NH_4OH—not merely the 1 per cent—will be neutralized when sufficient hydrochloric acid is added?

SUGGESTED READING

Journal of Chemical Education

JOHNSON, Electricity and Matter, **4,** 1088 (1927).

HUNT and BRISCOE, Factors Determining Electrolytic Dissociation, **6,** 1716 (1929).

HAZLEHURST, An Approach to the Theory of Ionization, **14,** 316 (1937).

DAVIDSON, Solutions of Electrolytes, **12,** 24 (1935).

WEST and GAHLER, The Apparent Degree of Ionization of Hydrochloric, Sulfuric and Acetic Acids, **19,** 366 (1942).

CHAPTER XVIII

TYPES OF CHEMICAL REACTIONS

Throughout the preceding chapters, numerous examples of chemical changes have been cited for the purpose of illustrating principles, characteristic types of chemical behavior, etc., and equations for these reactions have been written, usually by inspection. In all, however, only a relatively few reactions have been studied in detail. Before attempting any further study of individual chemical changes, it seems worth while to inquire into the manner in which different reactions are related one to the other. Just as classification of the chemical elements leads to simplification of study, so perhaps the various types of chemical reactions may be correlated to advantage.

OXIDATION-REDUCTION REACTIONS

So far as the reactions of inorganic substances are concerned, oxidation-reduction reactions constitute the single broadest, most inclusive, and certainly the most important type of chemical change. Historically, the terms *oxidation* and *reduction* owe their origin to certain practices in the chemical industries and from the modern point of view these terms are not entirely satisfactory. The term *oxidation* implies or at least suggests the element oxygen. However, oxygen may be but need not be involved in reactions of this type. Despite the fact that the two terms are somewhat misleading, they have become so firmly entrenched in the language of chemistry that they will undoubtedly continue to be used indefinitely.[1]

In the sections that follow, it will not be the purpose to make an exhaustive study of this particular type of reaction. A much more comprehensive treatment of oxidation and reduction is given in Chap. XXIV.

[1] In efforts to find more suitable designations for reactions of this type, numerous alternatives have been suggested. Thus, oxidation-reduction reactions are sometimes referred to as *electron change reactions*, *electronic reactions*, *electron exchange reactions* or *redox reactions*. It has also been suggested that the terms *de-electronation* and *electronation* be substituted for the terms *oxidation* and *reduction*, respectively. Although certain of these alternative designations have some merit, none has met with general acceptance.

18.1. Characteristics of Oxidation-reduction Reactions

Chemical changes classified as oxidation-reduction reactions may differ considerably so far as the nature of the reactants and products are concerned and yet have much in common with respect to the fundamental character of the changes involved. By definition, **an oxidation reaction is one in which atoms or radicals lose electrons.** Similarly, **a reduction reaction is one in which atoms or radicals gain (or acquire) electrons.**

Before proceeding with a study of specific cases, the student should have clearly in mind the following facts:

1. Oxidation and reduction always occur simultaneously and never independently. That is, an oxidation reaction, for example, cannot occur unless there occurs at the same time a reduction reaction.

2. In every oxidation-reduction reaction, one or more elements must undergo a change in valence.

3. The number of electrons gained in the reduction reaction must be identical with the number of electrons lost in the oxidation reaction.

4. By conventional practice, the element that loses electrons is said to be *oxidized* and, since the loss of electrons can occur only by virtue of the presence of an element that can accept those electrons, the element that gains or accepts the electrons is called the *oxidizing agent.*

5. Similarly, the element that gains electrons is said to be *reduced,* and the element that loses electrons is called the *reducing agent,* since by losing electrons it makes possible the occurrence of the reduction process. Thus, in any oxidation-reduction reaction, the oxidizing agent is reduced and the reducing agent is oxidized.

6. Oxidation-reduction reactions may involve substances that are ionic, covalent, or of intermediate types. Particularly in the case of predominantly covalent substances, the actual loss and gain of electrons may be more apparent than real. Nevertheless, since changes in valence are involved, there is no alternative but to classify these changes as oxidation-reduction reactions.

With these ideas as a background, it is now possible to review some of the reactions studied previously, to attempt to gain a better insight into the fundamental changes concerned, and to show why they are to be classified as oxidation-reduction reactions.

18.2. Reactions Involving Direct Union of Elements

Several reactions of this type have already been discussed, particularly in connection with the study of oxygen (Sec. 4.9). As an

additional example, consider the formation of bismuth bromide by the direct union of bismuth and bromine.

$$2Bi^0 + 3\overline{Br_2^0} \rightarrow 2Bi^{+++}Br_3^-.$$

This equation represents adequately the over-all change involved and can be balanced readily by trial and error if by no other means. However such an equation fails to show what occurs during the union of the elements concerned. Furthermore, many oxidation-reduction reactions are so complicated that the balancing of the corresponding equations requires the use of a systematic rather than a trial-and-error approach. Accordingly, it seems worth while to write the foregoing equation by a systematic method showing clearly the nature of the changes that occur.

In the reaction between bismuth and bromine, the bismuth atom loses its 3 electrons and, by definition, is thereby oxidized. Accordingly, the oxidation reaction may be represented as follows:

$$(a) \qquad Bi - 3e^- \rightarrow Bi^{+++}$$

Each bromine atom in the molecule of bromine (Br_2) is capable of gaining 1 electron, hence the reduction may be represented by

$$(b) \qquad Br_2 + 2e^- \rightarrow 2Br^-$$

However, it is readily seen that the number of electrons lost in (*a*) is different from the number gained in (*b*). Of course this may be remedied by multiplying equation (*a*) by 2 and multiplying equation (*b*) by 3, thus,

$$\begin{array}{ll} (a) & 2Bi - 6e^- \rightarrow 2Bi^{+++} \\ (b) & 3Br_2 + 6e^- \rightarrow 6Br^- \end{array}$$

Adding equations (*a*) and (*b*),

$$(c) \qquad 2Bi^0 + 3\overline{Br_2^0} \rightarrow 2Bi^{+++}Br_3^-$$

It is a common practice to indicate the valence of uncombined elements by zero superscripts and to set up the steps involved in writing the equation in the following form:

$$\begin{array}{ll} (a) & 2Bi^0 - 6e^- \rightarrow 2Bi^{+++} \\ (b) & \underline{3Br_2^0 + 6e^- \rightarrow 6Br^-} \\ (c) & 2Bi^0 + 3\overline{Br_2^0} \rightarrow 2Bi^{+++}Br_3^- \end{array}$$

The separation of the oxidation and reduction reactions and their representation as separate steps do not, of course, imply that they are independent processes.

A similar type of reaction but one involving the formation of a covalent compound is that shown by the following equation:

$$S^0 + \overline{O}_2^0 \rightarrow \overline{SO}_2$$

Sulfur dioxide is a predominantly covalent compound, and it is therefore improper to consider this reaction on exactly the same basis as in the case of the combination of bismuth and bromine. Since oxygen is electrically more negative than sulfur, one can adopt the viewpoint that in this reaction the sulfur atom acquires an "apparent positive valence" of four even though the sulfur atom may not actually lose electrons as is suggested by the oxidation reaction,

$$(a) \qquad S^0 - 4e^- \rightarrow \overset{\text{IV}+}{S}$$

To avoid the implication that sulfur ions are formed, the apparent positive valence of sulfur is indicated by the + sign and Roman numeral IV written *directly above* the symbol for sulfur. In a similar manner, the reduction reaction may be represented as follows,

$$(b) \qquad O_2^0 + 4e^- \rightarrow 2\overset{\text{II}-}{O}$$

Combining these two steps and adding, there obtains the expression,

$$\begin{array}{ll} (a) & S^0 - 4e^- \rightarrow \overset{\text{IV}+}{S} \\ (b) & O_2^0 + 4e^- \rightarrow 2\overset{\text{II}-}{O} \\ \hline (c) & S^0 + \overline{O}_2^0 \rightarrow S\overline{O}_2 \end{array}$$

This method of representing oxidation-reduction reactions may be applied in a similar fashion to other reactions involving the direct union of elements (see Exercises).

18.3. Displacement Reactions

In a manner comparable to that illustrated above, the equations for reactions previously cited in connection with the displacement of hydrogen from acids, water, and bases (Sec. 8.1) may now be rewritten as typical oxidation-reduction changes. Reactions involving displacement of elements other than hydrogen may be treated similarly.

Displacement of Hydrogen from Acids. The reaction between zinc and sulfuric acid,

$$Zn^0 + H_2^+SO_4^= \rightarrow Zn^{++}SO_4^= + \overline{H}_2^0$$

in which zinc is oxidized and hydrogen is reduced, may be written in the form,

$$
\begin{array}{ll}
(a) & Zn^0 - 2e^- \rightarrow Zn^{++} \\
(b) & 2H^+ + 2e^- \rightarrow H_2^0 \\
\hline
(c) & Zn^0 + 2H^+ \rightarrow Zn^{++} + H_2^0
\end{array}
$$

In this case, however, equation (*c*) does not present a complete picture since it does not show the origin of the hydrogen ions reduced in step (*b*). Accordingly, a fourth equation must be written to show that the hydrogen ions were supplied by sulfuric acid, thus,

$$(d) \qquad Zn^0 + H_2^+SO_4^= \rightarrow Zn^{++}SO_4^= + H_2^0$$

Development of the final form of this equation therefore involves four rather than three steps.

Displacement of Hydrogen from Water. The oxidation of magnesium and the reduction of hydrogen in the reaction between magnesium and hot water,

$$Mg + 2H_2O \rightarrow Mg^{++}(OH)_2^- + H_2^0$$

may be represented as an oxidation-reduction reaction as follows:

$$
\begin{array}{ll}
(a) & Mg^0 - 2e^- \rightarrow Mg^{++} \\
(b) & 2\overset{\mathrm{I+}}{H} + 2e^- \rightarrow H_2^0 \\
\hline
(c) & Mg^0 + 2\overset{\mathrm{I+}}{H} \rightarrow Mg^{++} + H_2^0 \\
(d) & Mg^0 + 2H_2O \rightarrow Mg^{++}(OH)_2^- + H_2^0
\end{array}
$$

In this reaction, hydrogen is the oxidizing agent and magnesium is the reducing agent.

Displacement of Hydrogen from Bases. Represented as an oxidation-reduction reaction, the interaction of aluminum and sodium hydroxide

$$2Al + 6Na^+OH^- \rightarrow 2Na_3^+AlO_3^\equiv + 3H_2^0$$

becomes

$$
\begin{array}{ll}
(a) & 2Al^0 - 6e^- \rightarrow 2\overset{\mathrm{III+}}{Al} \\
(b) & 6\overset{\mathrm{I+}}{H} + 6e^- \rightarrow 3H_2^0 \\
\hline
(c) & 2Al^0 + 6\overset{\mathrm{I+}}{H} \rightarrow 2\overset{\mathrm{III+}}{Al} + 3H_2^0 \\
(d) & 2Al^0 + 6Na^+OH^- \rightarrow 2Na_3^+(AlO_3)^\equiv + 3H_2^0
\end{array}
$$

In the compound $Na_3^+AlO_3^\equiv$, aluminum has an apparent positive valence of III, since the more negative oxygen atoms each have a valence of II⁻, ($3 \times \mathrm{II}^- = \mathrm{VI}^-$), and each of the more positive sodium atoms has a valence of I^+, ($3 \times \mathrm{I}^+ = \mathrm{III}^+$). Accordingly, the valence of Al must be III^+, since the compound must be electrically neutral.

18.4. Decomposition of Compounds

A very wide variety of reactions involving the decomposition of compounds must also be classified as oxidation-reduction reactions.

The products of such reactions may be the constituent elements, other compounds, or elements and compounds. The decomposition of potassium chlorate by means of heat (Sec. 3.3)

$$2KClO_3 \rightarrow 2KCl + 3O_2^0$$

will serve as a suitable illustration. Here, the apparent *positive* valence of chlorine in $KClO_3$ is V and in KCl the valence of chlorine is I^-. Hence, in this reaction, chlorine gains electrons. By loss of electrons, oxygen is oxidized from $\overset{II-}{O}$ to elemental oxygen in which the valence is considered to be zero.

$$\begin{array}{ll}
(a) & 6\overset{II-}{O} - 12e^- \rightarrow 3O_2^0 \\
(b) & 2\overset{V+}{Cl} + 12e^- \rightarrow 2Cl^- \\
\hline
(c) & 2\overset{V+}{Cl} + 6\overset{II-}{O} \rightarrow 2Cl^- + 3O_2^0 \\
(d) & 2KClO_3 \rightarrow 2K^+Cl^- + 3O_2^0
\end{array}$$

METATHETICAL REACTIONS

Quite apart from oxidation-reduction reactions that involve changes in valence is a class of reactions which may be represented by the general equation,

$$AB + CD \rightarrow AD + CB$$

wherein no change in valence occurs and the reaction simply takes place by a process amounting to "double displacement." Such chemical changes are usually called *metathetical reactions*,[1] and the over-all process is termed *metathesis*. In the sections that follow, the discussion of metathetical reactions will be restricted to those which occur *in dilute solutions at or near room temperature.*

18.5. Neutralization

Reactions between acids and bases are typical metathetical reactions as may be seen from the comparison,

$$\begin{gathered}AB + CD \rightarrow AD + CB \\ H^+Cl^- + Na^+(OH)^- \rightarrow H(OH) + Na^+Cl^-\end{gathered}$$

If a dilute solution of H^+ and Cl^- ions (hydrochloric acid solution) is added to a dilute solution of Na^+ and $(OH)^-$ ions (sodium hydroxide solution), the ensuing reaction produces *molecules* of the slightly

[1] In addition to the use of the term *metathetical*, reactions of this general type are variously referred to as *double decomposition reactions*, *ionic reactions*, *change-of-partner reactions*, etc. Since the literal meaning of the term *metathetical* is *displacement*, this term is perhaps no more suitable than any of the others.

ionized weak electrolyte H_2O, by virtue of the union of H^+ and $(OH)^-$ ions, thus,

$$H^+ + (OH)^- \rightarrow H_2O$$

The Na^+ and Cl^- ions, which were already present before the acid and base were mixed, are also present as such after the reaction (formation of H_2O) has gone to completion. *The salt Na^+Cl^- is not actually formed in the reaction.* The ions corresponding to this salt are present in the solution and, of course, solid crystals of Na^+Cl^- may be obtained by evaporation of the solvent. Thus, the essential change involved in this metathetical neutralization reaction is the formation of water, and this feature is common to all reactions between acids and bases in aqueous solution.

18.6. Reactions between Salts and Acids

The metathetical interaction of salts and acids may be illustrated by the following equation:

$$Ag^+(NO_3)^- + H^+Cl^- \rightarrow \underline{Ag^+Cl^-} + H^+(NO_3)^-$$

In this reaction, Ag^+ and Cl^- ions combine to form *insoluble* silver chloride without any actual change being experienced by the H^+ and $(NO_3)^-$ ions,

$$Ag^+ + Cl^- \rightarrow \underline{Ag^+Cl^-}$$

The insoluble silver chloride (the formula of which is underscored to indicate the formation of an insoluble precipitate) may be removed by filtration, and the resulting clear solution would exhibit all the properties of a dilute solution of nitric acid.

18.7. Reactions between Salts and Bases

The reaction between ammonium chloride and barium hydroxide serves as an example of this rather common and useful type of reaction,

$$2(NH_4)^+Cl^- + Ba^{++}(OH)_2^- \rightarrow 2(NH_4)(OH) + Ba^{++}Cl_2^-$$

The essential reaction in this case is the formation of the weak electrolyte NH_4OH,

$$(NH_4)^+ + (OH)^- \rightarrow (NH_4)(OH)$$

Barium and chloride ions are present as such both before and after the occurrence of the above reaction.

If ammonium sulfate were to be used in place of ammonium chloride,

$$(NH_4)_2^+ SO_4^= + Ba^{++}(OH)_2^- \rightarrow 2(NH_4)(OH) + Ba^{++}(SO_4)^=$$

all the ions concerned would be involved since

$$(NH_4)^+ + (OH)^- \rightarrow NH_4OH$$

and

$$Ba^{++} + (SO_4)^{=} \rightarrow \underline{Ba^{++}(SO_4)^{=}}$$

Thus one pair of ions unites to form a weak electrolyte, and the other pair actually combines to form an insoluble solid. Accordingly, it must be recognized that either one *or more* pairs of ions must combine during the occurrence of a metathetical reaction.

18.8. Reactions between Salts

This type of metathetical reaction may be illustrated by the interaction of silver nitrate and sodium chloride,

$$Ag^+(NO_3)^- + Na^+Cl^- \rightarrow \underline{Ag^+Cl^-} + Na^+(NO_3)^-$$

in which the essential change is the formation of insoluble silver chloride,

$$Ag^+ + Cl^- \rightarrow \underline{Ag^+Cl^-}$$

By comparison with the reaction between silver nitrate and hydrochloric acid solution (Sec. 18.6), it will be seen that these two metathetical reactions are fundamentally the same since they both occur for the same reason, *viz.*, the union of silver and chloride ions.

Another example of this type of reaction is that between lead nitrate and potassium acetate,

$$Pb^{++}(NO_3)_2^- + 2K^+(C_2H_3O_2)^- \rightarrow Pb(C_2H_3O_2)_2 + 2K^+(NO_3)^-$$

a reaction that occurs because of the union of lead and acetate ions to form molecules of the slightly ionized weak electrolyte, lead acetate.

18.9. Factors Involved in the Occurrence of Metathetical Reactions

The preceding examples are sufficient to show that a metathetical reaction will occur when the concentration of one or more pairs of ions is decreased as a result of the formation of a weak electrolyte or an insoluble substance. It is also of importance not only to recognize that certain metathetical reactions will occur, but also to be able to estimate the extent to which such reactions will proceed to completion. The chemist is frequently faced with the problem of predicting whether a given metathetical reaction will occur at all and, if so, whether it will proceed to completion.

Consider, for example, the reaction between mercuric nitrate and sodium cyanide,

$$Hg^{++}(NO_3)_2^- + 2Na^+(CN)^- \rightarrow Hg(CN)_2 + 2Na^+(NO_3)^-$$

One would predict that this reaction will occur because the concentration of a pair of ions [Hg^{++} and $(CN)^-$] will be decreased owing to the formation of the weak electrolyte, mercuric cyanide. Further, since $Hg(CN)_2$ is a very weak electrolyte, substantially all of the Hg^{++} and $(CN)^-$ ions will become tied up in the form of molecules of mercuric cyanide and the reaction will proceed essentially to completion.

Similarly, one would predict that the reaction between copper nitrate and phosphoric acid,

$$3Cu^{++}(NO_3)_2^- + 2H_3(PO_4) \rightarrow \underline{Cu_3^{++}(PO_4)_2^{\equiv}} + 6H^+(NO_3)^-$$

would not only occur but would also go to completion owing to the fact that copper phosphate is very insoluble and its formation results in a decrease in the concentration of copper and phosphate ions in the solution.

On the other hand, consider the equation for a proposed reaction between magnesium acetate and ammonium chloride.

$$Mg^{++}(C_2H_3O_2)_2^- + 2(NH_4)^+Cl^- \rightarrow Mg^{++}Cl_2^- + 2(NH_4)^+(C_2H_3O_2)^-$$

It may be seen that this reaction will not occur since neither a weak electrolyte nor an insoluble substance is formed. Hence, the total ion concentration will not be changed upon bringing together solutions of these two salts.

Accordingly, the problem of deciding whether a given metathetical reaction will occur involves the ability to recognize (*a*) weak electrolytes and (*b*) insoluble substances. Information relative to common acids, bases, and salts that are classified as weak electrolytes has already been provided (Sec. 17.6), and some general rules relating to solubility relationships are outlined in the following section. Once the fact that a metathetical reaction will occur has been established, it must be recognized that the extent to which it will proceed toward completion is dependent upon the properties of the substance the formation of which is responsible for the occurrence of the reaction. If a metathetical reaction occurs because of the formation of a weak electrolyte, the weaker the electrolyte the more nearly will the reaction proceed to completion. Similarly, if the formation of an insoluble substance is involved, the more insoluble the substance, the greater the extent of reaction. Hence, it is concluded that "completion" of metathetical reactions is dependent upon the effectiveness of weak

electrolyte or insoluble product formation in decreasing the concentration of at least one pair of ions.

18.10. Solubilities of Common Acids, Bases, and Salts

Before studying the following generalizations with respect to solubility relationships, the student should review Sec. 9.5.

It must be recognized at the outset that any effort to classify solutes in relation to the extent to which they dissolve in a solvent such as water is likely to be none too successful owing to wide variations in solubility and to difficulties involved in deciding just where to draw a line of demarcation between substances which are to be considered as soluble and those which are to be looked upon as insoluble. Nevertheless, it is possible to set up a few general rules to serve as a practical working basis for the purpose at hand as well as for certain other purposes. The generalizations given below relate *only* to solubility in water at room temperature.

Acids. All *common* acids are *soluble* with the exception of silicic acid [$H_2(SiO_3)$], and arsenious acid [$H(AsO_2)$].

Bases. All *common* bases are *insoluble* with the exception of the following:

$$\left.\begin{array}{l}\text{Ammonium hydroxide } (NH_4OH)\\ \text{Sodium hydroxide } (NaOH)\\ \text{Potassium hydroxide } (KOH)\end{array}\right\}\text{extensively soluble}$$

$$\left.\begin{array}{l}\text{Calcium hydroxide } [Ca(OH)_2]\\ \text{Strontium hydroxide } [Sr(OH)_2]\\ \text{Barium hydroxide } [Ba(OH)_2]\end{array}\right\}\text{sparingly soluble}$$

Salts. All *common* sodium, potassium, and ammonium salts are extensively *soluble.*

All silver salts are *insoluble* except silver fluoride (AgF), silver nitrate [$Ag(NO_3)$], and silver chlorate [$Ag(ClO_3)$]. Silver acetate [$Ag(C_2H_3O_2)$] and silver sulfate [$Ag_2(SO_4)$] are only *sparingly soluble.*

All nitrates, acetates, and chlorates are extensively soluble except silver acetate (see above).

All *normal* sulfates are *soluble* except lead sulfate [$Pb(SO_4)$], strontium sulfate [$Sr(SO_4)$], and barium sulfate [$Ba(SO_4)$], which are *insoluble* and mercurous sulfate [$Hg_2(SO_4)$] and silver sulfate [$Ag_2(SO_4)$], which are only *sparingly soluble.*

All chlorides are *moderately to extensively soluble* except silver chloride (AgCl) and mercurous chloride (Hg_2Cl_2). Lead chloride ($PbCl_2$) is only slightly soluble.

All *normal* sulfides, carbonates, sulfites, silicates, and phosphates are *insoluble* except those of sodium, potassium, and ammonium.

In general, *acid salts* are *soluble.*

As the student acquires more and more information concerning the specific properties of individual chemical compounds, it is inevitable that some exceptions to the foregoing generalizations will be encountered.

EXERCISES

1. Define the following terms: (*a*) oxidation, (*b*) oxidizing agent, (*c*) reducing agent, (*d*) reduction.

2. List the characteristic features of oxidation-reduction reactions.

3. Why must oxidation and reduction reactions always occur together?

4. What is the most important distinction between oxidation-reduction reactions and metathetical reactions?

5. Write (in steps) equations for the following oxidation-reduction reactions:

(*a*) The direct union of
  (1) Lead and sulfur
  (2) Magnesium and oxygen
  (3) Sulfur dioxide and oxygen
  (4) Carbon and sulfur
  (5) Hydrogen and oxygen

(*b*) The decomposition (by application of heat) of
  (1) Potassium nitrate
  (2) Mercuric oxide
  (3) Lead dioxide
  (4) Manganese dioxide

(*c*) The displacement of hydrogen by the interaction of
  (1) Zinc and hydrochloric acid
  (2) Magnesium and acetic acid
  (3) Lead and sulfuric acid
  (4) Calcium and phosphoric acid
  (5) Sodium and water
  (6) Iron and water (steam)

(*d*) The displacement reaction between zinc metal and copper sulfate solution.

(*e*) The production of elemental metals by the reactions between
  (1) Copper oxide and hydrogen
  (2) Ferric oxide and hydrogen
  (3) Ferric oxide and carbon monoxide
  (4) Lead monoxide and carbon monoxide

6. Under what conditions will a metathetical reaction occur?

7. If a metathetical reaction will occur, what determines the extent to which it will go to completion?

8. Of the following pairs of similar metathetical reactions, indicate in each case which will proceed most nearly to completion and cite reasons for the answer in each case:

  (*a*) Sodium sulfate + silver nitrate
  (*b*) Sodium sulfate + lead nitrate

  (*a*) Potassium sulfide + sulfuric acid
  (*b*) Potassium cyanide + sulfuric acid

(*a*) Hydrochloric acid + barium hydroxide
(*b*) Hydrobromic acid + barium hydroxide

9. Write equations for the following indicated reactions. In each case, mark all strong electrolytes, all insoluble substances, predict whether the reaction will occur, and state the basis for each prediction:

(*a*) Lead nitrate + hydrochloric acid
(*b*) Strontium chloride + ammonium acetate
(*c*) Copper sulfate + sodium phosphate
(*d*) Mercuric nitrate + sodium cyanide
(*e*) Zinc chloride + potassium sulfate
(*f*) Phosphoric acid + aluminum hydroxide
(*g*) Nickel nitrate + sodium iodide
(*h*) Ferric chloride + potassium thiocyanate
(*i*) Ammonium sulfate + sodium hydroxide
(*j*) Lead chloride + sodium acetate

SUGGESTED READING

Journal of Chemical Education

HEIMERZHEIM, Solubility Generalizations, **18**, 377 (1941).

Industrial and Engineering Chemistry

KOBE and DEIGLMEIER, Strontium Carbonate—Conversion from Strontium Sulfate by Metathesis with Alkali Carbonate Solutions, **35**, 323 (1943).

See references at end of Chap. XXIV.

CHAPTER XIX

COLLOIDS

Emphasis has already been placed upon the properties of matter in each of the three physical states and in solutions. There remain to be considered the characteristics of solids, liquids, and gases in a state of existence known as the *colloidal condition* or *colloidal state*. The various combinations of solids and liquids, liquids and liquids, liquids and gases, etc., in the colloidal condition are called *colloids* and exhibit certain similarities to true solutions. On the other hand, colloids and solutions differ in many important respects.

19.1. Nature of Colloids

The term *colloid* is derived from the Greek work *kolla* which means glue, a term rather generally suggestive of the character of many (but not all) colloids. The term *colloid* is applied to many intimate mixtures of two or more substances which are usually very finely divided and mutually insoluble. Perhaps the best means of gaining some idea as to the over-all nature of those materials commonly classified as colloids is to cite some familiar examples. Such common materials as milk, ink, egg white, gelatin, glue, soap, "milk of magnesia," and many foodstuffs, medicinals, etc., are colloidal in character. Processes such as the treatment of municipal water supplies, sewage disposal, preparation of soils for road building, drilling of oil wells, manufacture of clay products, and smoke abatement, either involve the use of colloidal materials or are dependent upon a knowledge of the properties of matter as it exists in the colloidal condition.

Distinction between Colloids and Solutions. From the recognition that confusion is likely to result from certain similarities between colloids and solutions, it seems necessary to draw a clear distinction between the two before proceeding with any detailed study of colloids.

It will be recalled that a true solution consists of a solvent in which is dissolved a solute in the form of units which usually are not larger than single molecules. Frequently when two true solutions are mixed, these molecules react to form an insoluble solid, the molecules of which collect to form particles large enough to settle to the bottom of the container under the influence of gravity. But occasionally one finds

that the insoluble solid particles that form are so small that they either settle out extremely slowly or remain suspended in the liquid indefinitely. Such a system, consisting of very small particles of a solid suspended throughout the body of a liquid, is classed as a colloid. The suspended particles of solid are larger than single molecules and consist of clusters of molecules or atoms which, for reasons which will be indicated later, remain suspended in the liquid.

A similar result may also be realized by starting with a large particle of a solid and subdividing this solid until the particles become so small that they will remain in suspension. For example, a cube of gold having edges 1 cm. in length and therefore an exposed surface area of 6 sq. cm. would, of course, not remain suspended in water. If, however, this cube is divided into cubes having edges only 0.01 cm. in length, the total number of such cubes would be $100 \times 100 \times 100$ or 10^6 cubes. Since each of these cubes has a surface area of

$$6 \times (0.01)^2 = 6 \times 10^{-4} \text{ sq. cm.},$$

the total surface area exposed by all these cubes would be

$$10^6 \times 6 \times 10^{-4} = 600 \text{ sq. cm.},$$

an area one hundred times as great as that of the original cube. Upon being mixed with water, cubes of this size would also settle to the bottom of the container but, if the process of subdivision were continued until the cubes were so small that the total exposed surface area were about one million times as great as that of the original cube, the particles would then be so small that they would remain suspended in water in the colloidal condition. This process of subdivision would, of course, involve a tremendous increase in exposed surface (as compared with that of the original cube) and, as will be shown later, this fact has an important bearing upon the properties of matter in the colloidal state.

Dimensions of Colloidal Particles. With reference to the preceding example, it becomes of interest to calculate the number of cubes into which the original cube would have to be subdivided in order to produce colloidal gold. Since the *average* diameter of colloidal particles is *approximately* 10^{-6} cm., the required number of cubes would be $10^6 \times 10^6 \times 10^6 = 10^{18}$ cubes, each having edges 10^{-6} cm. in length and a surface area of $6 \times (10^{-6})^2$ or 6×10^{-12} sq. cm. Accordingly, the total area exposed by the 10^{18} cubes would be

$$10^{18} \times 6 \times 10^{-12} = 6 \times 10^6 \text{ sq. cm.},$$

or, as indicated above, an area one million times as great as that of the original cube and about one-seventh the area of a football field.

Although the dimensions of colloidal particles could be expressed in centimeters or millimeters, there has been adopted another unit, the *millimicron*, more suited to the expression of small lengths. The millimicron is represented by the symbol $m\mu$, and is equal to one one-millionth of a millimeter (*i.e.*, 10^{-6} mm.).

The largest known molecules have diameters of approximately 1 $m\mu$; hence, any particle having a diameter of 1 $m\mu$, or less, would exist in water (or other solvent) in true solution. Particles having diameters within the range of 1 to 100 $m\mu$ are, in general, considered to be of colloidal size. Particles of diameter greater than 100 $m\mu$ would, in general, be too large to remain suspended in the colloidal condition. Incidentally, particles having diameters of about 150 $m\mu$ represent the smallest objects that can be seen by means of an ordinary microscope. The foregoing relationships may be clarified by the accompanying chart.

DIMENSIONS OF PARTICLES OF MATTER

		1 $m\mu$	100 $m\mu$
Approximate diameter	←	←——→	→
Nature of particles	Molecules Atoms Ions	Colloidal	Larger than colloidal
Mode of existence in presence of a solvent	In true solution	In colloidal suspension	Settle under influence of gravity

Types of Colloids. From the preceding discussion, it becomes rather apparent that a colloidal system must consist of a mixture of at least two materials. By analogy with the various possible varieties of true solutions, it would appear that nine combinations might be possible. However, since mixtures of gases are always homogeneous and mutually soluble, colloidal systems consisting of gases in gases are not possible. Of the eight remaining theoretically possible colloidal systems several are relatively uncommon.

In the language of the chemistry of colloids, the particles (solid, liquid, or gas) and the medium (solid, liquid, or gas) in which the particles exist in the colloidal condition are known as *phases*. The colloidal particles are referred to as being the *dispersed phase*, and the medium in which they are dispersed is called the *dispersion medium*. In terms of these two components, the most common types of colloidal systems are listed in Table 24.

Before leaving the subject of the general nature of colloidal materials, it should be understood clearly that the existence of matter in the colloidal condition is largely independent of the *kind* of matter involved. For example, many chemical substances that exist in water in the form

of true solutions under one set of experimental conditions will, under another set of conditions or in another liquid, exist in the colloidal condition. The properties of matter in the colloidal state are largely dependent upon the *state of subdivision* of the colloidally dispersed materials.

TABLE 24

COMMON TYPES OF COLLOIDAL SYSTEMS

Dispersed phase	Dispersion medium	Example
Solid..............	Liquid	Colloidal gold in water
Solid..............	Gas	Smoke (particles of carbon in air)
Liquid............	Gas	Fog (water droplets in air)
Liquid............	Liquid	Emulsions (such as oil in water)
Gas...............	Liquid	Foams

19.2. Preparation of Colloids

The available methods whereby colloids may be produced have already been suggested (Sec. 19.1) and may be classified broadly as *condensation* methods and *dispersion* methods.

Condensation. As is suggested by the term itself, condensation methods involve starting with single molecules and bringing them together in sufficient number to build up particles having diameters within the range of 1 to 100 mμ. A familiar example of the application of this method is found in the formation of a fog or mist by the rapid expansion of moist air. Upon being cooled by expansion (Sec. 6.2), the water molecules collect to form small droplets of colloidal size. By striking an electric arc between metal electrodes held under water or other suitable liquid, the metal is vaporized by the arc and the vapors condense to form particles many of which are within the range of the dimensions of colloidal particles. Lead, silver, copper, platinum, gold, and other metals have been dispersed successfully by this procedure. Colloidal gold may be so produced in such a finely subdivided condition that the colloidal particles will settle (under the influence of gravitational attraction) only through a distance of a little more than 1 cm. over a period of 10 years.

This process of building up colloidal particles from single molecules, atoms, or ions, is perhaps most commonly illustrated by reactions between electrolytes in true solutions. Yellow colloidal arsenious sulfide may be formed by the metathetical reaction between arsenious acid and hydrogen sulfide.

$$2H_3^+AsO_4^{\equiv} + 3H_2S \rightarrow 6H_2O + \underline{As_2S_3}_{(colloidal)}$$

Similarly, reddish-brown colloidal ferric hydroxide may be produced by the metathetical reaction between ferric chloride and water,

$$Fe^{+++}Cl_3^- + 3H_2O \rightarrow 3H^+Cl^- + \underline{Fe(OH)_{3(colloidal)}}$$

Oxidation-reduction reactions also may be employed. Thus, brown or black colloidal nickel may be formed by heating a solution of nickel carbonyl in benzene.

$$\begin{array}{ll} (a) & 4(\overset{\text{I}-}{CO}) - 4e^- \rightarrow 4CO \\ (b) & \overset{\text{IV}+}{Ni} + 4e^- \rightarrow Ni^0 \\ \hline (c) & Ni(CO)_4 \rightarrow 4CO + \underline{Ni^0{}_{(colloidal)}} \end{array}$$

Colloidal sulfur may be prepared by the interaction of hydrogen sulfide and sulfurous acid.

$$\begin{array}{ll} (a) & 2S^{=} - 4e^- \rightarrow 2S^0 \\ (b) & \overset{\text{IV}+}{S} + 4e^- \rightarrow S^0 \\ \hline (c) & 2S^{=} + \overset{\text{IV}+}{S} \rightarrow 3S^0 \\ (d) & 2H_2S + H_2SO_3 \rightarrow 3H_2O + \underline{3S^0{}_{(colloidal)}} \end{array}$$

Many other metathetical and oxidation-reduction reactions may be employed similarly in condensation methods for the preparation of elements or compounds in the colloidal condition.

Dispersion. The process of producing colloids by starting with large particles and breaking them down into particles of colloidal size is known as *dispersion* or *peptization.* This type of method is illustrated by the following examples:

1. In recent years mechanical grinding machines (*colloid mills*) have been invented for this purpose and are remarkably effective in producing colloidal particles having diameters as small as 5 mμ.

2. Colloids consisting of liquids dispersed in liquids may sometimes be prepared merely by shaking the two liquids together either manually or by mechanical agitation. Mixtures of butterfat and milk may be rendered colloidally homogeneous ("homogenized") by subjecting the mixture to high pressures and forcing the mixture through a very fine orifice. The fat globules are thereby dispersed uniformly throughout the body of the liquid milk.

3. In one sense, the production of colloidal metals by the use of an electric arc may be classified as a dispersion method since dispersion of the metal in the form of vapor must necessarily precede condensation of these vapors.

4. Some substances are peptized merely by contact with a suitable dispersion medium. For example, materials such as glue and gelatin

are peptized upon contact with water and thereupon assume a colloidal condition rather than dissolving to form true solutions. Similarly, when one attempts to wash (with water) freshly precipitated zinc sulfide on an ordinary filter paper, the sulfide is frequently peptized by the water and the colloidal particles pass through the small pores in the filter paper.

19.3. Purification of Colloids

The stability of a colloid is often influenced adversely by the presence of molecules or ions dissolved in the dispersion medium. Consequently, in order to stabilize a colloid, it may become necessary to

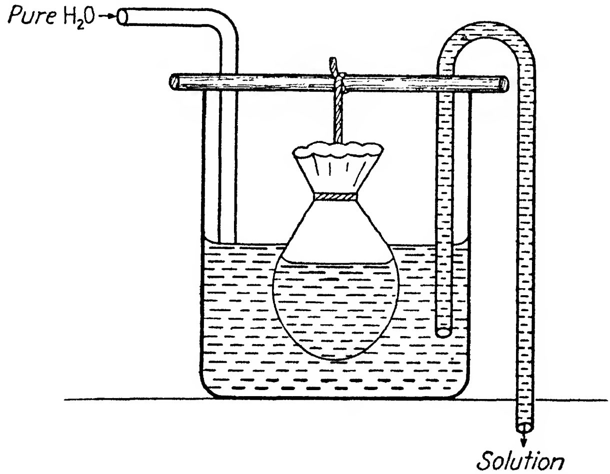


FIG. 83.—A simple illustration of the process of dialysis.

subject it to a purification process known as *dialysis*. This procedure is carried out by enclosing the colloidal system in a membrane such as parchment paper or collodion, and immersing the bag and its contents in pure solvent, *e.g.*, water, as shown in Fig. 83. The dissolved impurities diffuse through the membrane and may be progressively removed by providing for continuous introduction of fresh water. Owing to the fact that either the membrane is selectively permeable only by solute particles or that the solute particles diffuse much more rapidly than the larger colloidal particles, an extended dialysis is frequently very effective as a means of purification. This method is used largely in the purification of colloids consisting of solids dispersed in liquids.

19.4. Properties of Matter in the Colloidal Condition

Two important characteristics of colloids have already been considered, *i.e.*, the dimensions of colloidal particles and the tremendous

surface area exposed by a given weight of matter in the colloidal condition. Several other properties are, in some measure, shared by colloids in general, and these properties are useful in identifying and characterizing colloids.

Tyndall Effect. When a strong beam of light is passed through a solution, the path of the beam is not visible to the unaided eye. If, however, this beam of light is passed through a colloid, the small col-

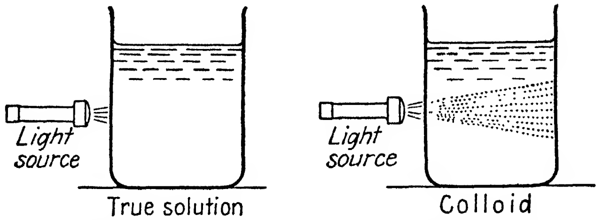


FIG. 84.—Tyndall effect. The path of a beam of light appears as a Tyndall cone in the case of a colloid but not in the case of a true solution.

loidal particles act as reflectors and the path of the beam is visible as a turbid cone (Fig. 84). Named for the scientist who first observed and described it, this phenomenon is known as the *Tyndall effect* and the visible path of the light is known as a *Tyndall cone*. The same sort of effect is commonly observed when a beam from a searchlight passes through a fog, mist, or smoke.

Brownian Movement. If a Tyndall cone is viewed through a microscope placed at right angles to the beam of light, the motion of the light reflected from the colloidal particles gives evidence that the particles are in motion (Fig. 85). Such a device is known as an *ultramicroscope* and enables the observer to view the unordered motion of colloidal particles which are not much larger than some molecules. This motion of colloidal particles was first observed in 1827 by the Scotch botanist, Robert Brown, and has since been known as *Brownian movement*. As a result of his studies of the Brownian movement by means of an ultramicroscope, the French chemist, Jean Perrin, found it possible to measure directly the size, mass, and velocity of motion of certain colloidal particles. From these data, the kinetic energies of the particles were calculated. Perrin found that, *at any given temperature, the average kinetic energy is the same for particles of widely different mass and of the same order of magnitude as the average kinetic energy of gas*

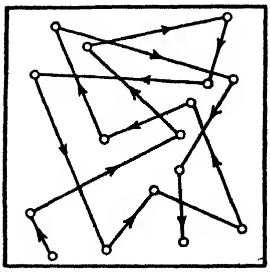


FIG. 85.—Illustration of Brownian movement.

molecules at the same temperature. It is of interest to consider these striking results in the light of the kinetic-molecular theory (Sec. 5.2) and to recognize that the inherent kinetic energy of the individual particles is an important factor bearing upon the stability of colloidal systems.

Electrical Properties. When a colloid is placed in the space between two electrodes arranged in a cell, such as that shown in Fig. 86, and a relatively high voltage is employed, the colloidal particles migrate slowly toward either the positive or the negative electrode. Colloidal metals and metal sulfides usually migrate toward the positive electrode; hence, it is concluded that these particles must bear a *negative* charge. Correspondingly, most colloidal hydroxides of the metals move toward the negative electrode, a fact that indicates that these

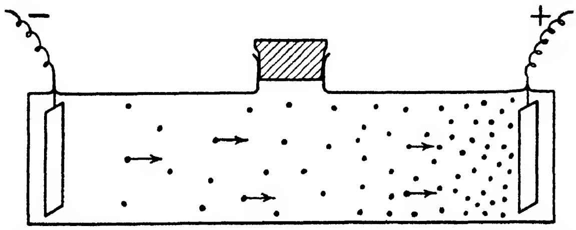


FIG. 86.—Migration of negatively charged colloidal particles.

colloidal particles bear a *positive* charge. The magnitude of the electrical charges borne by colloidal particles is far greater than the charges of individual ions, and the relatively slow migration of these particles is attributed to their relatively great size. Since colloidal particles usually consist of clusters of *electrically neutral* atoms or molecules, there arises immediately a question as to the origin of the charges possessed by colloids. The answer to this question requires some additional information concerning the subject of adsorption.

Adsorption. Although the molecules in the interior of a colloidal particle are attracted equally in all directions by other molecules, those on the surface of a colloidal particle are in a condition similar to that experienced by molecules in the surface of a liquid (Sec. 6.3), *i.e.*, they are subject to unequal forces of attraction. Since colloidal particles possess great surface area, there are many such molecules in the surface of a single particle. These molecules, therefore, are capable of attracting and holding other molecules, atoms, or ions. The ability of colloidal particles and other finely divided forms of matter to attract and hold molecules, atoms, or ions on their surfaces is known as *adsorption.* The property of adsorption plays an important role in many processes including the adsorption of poisonous gases on the charcoal contained

in gas masks, the flotation of ores (Sec. 26.2), the bleaching of cottonseed oil by means of fuller's earth, etc.

Suspensoids. The electrical charge borne by colloidal particles is due to the adsorption of ions from the surrounding medium. As is true of adsorption in general, the adsorption of ions by colloidal particles is highly selective. That is, a given colloidal particle may adsorb positive ions and not negative ions, while with other kinds of colloids, the reverse is true. Since colloidal particles of any particular kind all adsorb ions of the same charge, these particles tend to prevent coagulation and hence contribute to the stability of colloidal systems. *Colloids in which the dispersed phase consists of particles that selectively adsorb ions from the dispersion medium are known as suspensoids.* The viscosity of a suspensoid is usually not greatly different from the viscosity of the dispersion medium.

Emulsoids. In contrast to suspensoids, there are colloids which are less selective with regard to the adsorption of ions and which exhibit a marked tendency to adsorb molecules of the dispersion medium. Such colloids are known as *emulsoids.* As the particles continue to adsorb molecules of the dispersion medium, they appear to swell, and this swelling process may continue until the entire system assumes a semirigid condition such as exists in glues, jellies, etc. This swelling process is commonly observed when dried fruits are placed in contact with water. In semiarid regions, certain forms of plant life retain moisture over long periods of time because they contain colloids that are capable of adsorbing water to an unusual extent. In any event, the extent of adsorption of the dispersion medium depends upon the specific character of the emulsoid, the temperature, and the acidity of the environment. It is rather apparent that the viscosity of an emulsoid is usually much greater than that of the dispersion medium.

19.5. Jellies and Gels

The adsorption of molecules of the dispersion medium by the colloidal particles in an emulsoid may continue until most of the dispersion medium has been adsorbed. As this process continues, the colloid becomes increasingly viscous and finally sets to a semirigid mass which is commonly described by the term *jelly.* Familiar examples include fruit jellies, in which a substance known as *pectin* yields the emulsoid particles that adsorb the colored and sweetened water solution serving as the dispersion medium. Jelly formation is involved also in the preparation of gelatin desserts.

If the dispersion medium is removed from a jelly, the resulting amorphous solid material frequently possesses a very porous structure

and is called a *gel*. If water or alcohol, for example, is the dispersion medium, a jelly may sometimes be converted to a gel simply by cautious application of heat. Silica gel (SiO_2) and alumina gel (Al_2O_3) may be produced in this manner. Gels commonly have a structure somewhat like that of a sponge or honeycomb. Accordingly, gels present relatively great exposed surfaces and are rather commonly used as carriers for catalysts, as deodorants, and as adsorbents for other purposes.

19.6. Coagulation of Colloids

Colloids are produced in the laboratory and commercially because such substances possess useful properties. On the other hand, it is frequently true that in an effort to form precipitates, the objective is not realized because the material desired in the form of a precipitate actually appears in the colloidal condition. Consequently, it may be just as important to know how to destroy (or coagulate) colloids as it is to know how to produce them. Disturbance of those factors which are responsible for the stability of a colloid usually results in coagulation (or precipitation). In general, suspensoids are more easily coagulated than emulsoids.

Coagulation of Suspensoids. Since the electrical charge borne by suspensoid particles is the chief factor responsible for the stability of suspensoid colloids, neutralization of this charge usually results in precipitation. Addition of an electrolyte that furnishes ions of charge opposite to that of the charge borne by the suspensoid particles is commonly effective in causing coagulation at ordinary temperatures and more effective at elevated temperatures. Upon neutralization of the charges on the suspensoid particles, there is no longer an electrical repulsion of one particle by another, and the particles collect upon collision until the Brownian movement is no longer capable of keeping these enlarged particles in suspension. Elevation of the temperature serves to increase the kinetic energy of the particles which results in increased frequency of collision and consequently accelerates the coagulation process. The valence of the ion of the precipitating electrolyte has a marked bearing upon its efficiency. A divalent ion is many times more effective than a univalent ion, and a trivalent ion is often hundreds of times more effective than a univalent ion. Thus, in the coagulation of the negatively charged particles of arsenious sulfide, aluminum ion (Al^{+++}) would be more effective than calcium ion (Ca^{++}), which in turn would be more effective than sodium ion (Na^{+}).

If suspensoids of opposite charge are brought together, coagulation usually occurs as the result of *mutual* neutralization of charges. Thus,

the mixing of a positively charged ferric hydroxide suspensoid and a negatively charged arsenious sulfide suspensoid results in precipitation of both.

Coagulation of Emulsoids. The stability of an emulsoid is due to (*a*) the electric charge borne by the emulsoid particles and (*b*) the layers of adsorbed dispersion medium on the surface of the emulsoid particles. The coagulation of emulsoids may be accomplished by elimination of the factors responsible for their stability. For example, if water is the dispersion medium, the emulsoid particles may often be stripped of adsorbed molecules by an elevation of temperature (boiling) or by the addition of a dehydration agent such as alcohol. Once this has been accomplished, neutralization of the electrical charge usually results in complete coagulation. Sometimes, heating alone will accomplish coagulation; in other cases the addition of a dehydrating agent (without heating) is effective.

19.7. Emulsions

When two mutually insoluble liquids, such as kerosene and water, are thoroughly shaken together, the resulting mixture consists of tiny droplets of the two liquids dispersed throughout each other. Owing to the surface tension forces (Sec. 6.3) that cause liquids to tend to present the least possible exposed surface, the small drops of kerosene and water will, upon standing, coalesce into larger and larger drops until finally the water and kerosene separate into two distinct layers. Frequently the addition of a third substance will stabilize the dispersion to such an extent that the tiny drops remain dispersed. Such a colloidal dispersion of one liquid in another is called an *emulsion*. The stabilizing action of the added substance usually depends upon its ability to lower the surface tension of the liquids concerned. Substances employed in the stabilization of emulsions are known as *emulsifying agents*. Occasionally stable emulsions are produced when two liquids are mixed because one of the liquids contains an impurity that acts as an emulsifying agent.

Numerous examples of useful emulsions might be cited. Milk, mayonnaise, certain lubricants, etc., are familiar examples. Soap is rather commonly used as the emulsifying agent in the formation of oil-water emulsions. If a sodium soap is employed, the oil will be dispersed throughout the body of the water, while use of a calcium soap results in an emulsion in which the water is the dispersed phase and the oil is the dispersion medium. The cleansing action of a soap is an interesting example of the formation of emulsions. The dirt on the hands, for instance, is usually surrounded by a thin film of grease or oil. Pure water does not emulsify this oil or grease, but soap

lowers the surface tension between the water and oil and thus results in the formation of a stable emulsion which encloses the particles of dirt, and the whole may then be rinsed away with water.

19.8. Applications of Colloids

At various points in the preceding discussion, numerous examples of the use of materials in the colloidal condition have been cited. Some additional applications of considerable importance remain to be considered.

Smoke Abatement. Smoke consists of fine particles of carbon dispersed colloidally in a gaseous dispersion medium, the air. The problem of eliminating smoke nuisances resulting from smoke production in chemical and other manufacturing plants, particularly where bituminous coal is used as a fuel, was solved by the American chemical engineer, F. G. Cottrell, in 1911. The Cottrell process involves passing the smoke between two electrically charged plates. The charged colloidal particles are attracted to the plate bearing the opposite charge and, upon neutralization of the charge borne by the particles of carbon, they coagulate to form grains too large to exist in the colloidal condition. This results not only in the substantially complete elimination of the smoke nuisance but also in the recovery of considerable quantities of carbon which may be used as a fuel or for other purposes.

Formation of Deltas. When the muddy waters of a fresh-water stream flow into a body of "salt water," the colloidal materials in the muddy water are precipitated by the high concentration of dissolved electrolytes in the sea water. Thus, the vast reaches of the Mississippi delta region have been built up, at least in part, by the coagulating action of electrolytes present in the waters of the Gulf of Mexico. This factor has, therefore, an important bearing on the navigability of waters near the mouths of rivers.

Vital Processes. The subject of colloid chemistry is particularly important to students of botany, biology, and medicine, since all vital processes of plants and animals are intimately concerned with colloidal materials. The germination of seed, the growth of plants, and the very structure of the plants themselves involve complex colloidal materials to a predominant extent. The protoplasm that is the basis of all animal life is essentially colloidal in character. Furthermore, most foodstuffs essential to the maintenance of animal life are colloids of one kind or another.

Protective Colloids. In the commercial production of colloidal products, stabilization is often accomplished by addition of so-called *protective colloids*, which are usually emulsoids. Thus, in forming mayonnaise salad dressing an emulsion of a salad oil (olive oil, cotton-

seed oil, etc.) in vinegar (a dilute water solution of acetic acid) is stabilized by the addition of egg yolk. The smooth texture of good-quality ice cream may be produced by adding gelatin which serves as a protective colloid, while gum arabic serves the same purpose in marshmallows. In the manufacture of india ink, colloidal carbon is stabilized by the use of protective colloids consisting of various gums. Certain useful lubricants consist of colloidal graphite stabilized by tannin, a protective colloid which also finds extensive use in the ceramic industries.

EXERCISES

1. What is the essential difference between (*a*) suspensoids and emulsoids, (*b*) emulsoids and emulsions, (*c*) colloids and true solutions, (*d*) jellies and gels?

2. Define the following terms: (*a*) dialysis, (*b*) protective colloid, (*c*) emulsifying agent, (*d*) ultramicroscope, (*e*) Tyndall effect, (*f*) Brownian movement, (*g*) millimicron, (*h*) dispersed phase, (*i*) dispersion medium, (*j*) adsorption.

3. Make a list of at least 10 natural or artificial materials that are colloidal in character.

4. With regard to colloids, list methods that are practically useful in (*a*) preparation, (*b*) purification, (*c*) stabilization, and (*d*) coagulation, and indicate briefly the characteristic features of these methods.

5. Draw an enlarged diagram of an emulsoid particle in a manner that will serve to explain why the addition of an electrolyte might fail to coagulate such a colloid.

6. To what properties do the various types of colloids owe their stability?

7. In what respects are colloidal particles and gas molecules similar?

8. In the study of colloids, why is the property of viscosity of importance?

9. What is meant by the mutual precipitation of colloids?

10. If a negative colloid is to be precipitated by the addition of an electrolyte which, of course, furnishes both positive and negative ions, why is it that the addition of negative ions does not further stabilize the colloid and thus counteract the precipitating action of the positive ions?

11. If one wished to coagulate a positive colloid by the addition of an electrolyte, what electrolytes would be most effective?

SUGGESTED READING

Journal of Chemical Education

McBain, Structure in Amorphous and Colloidal Matter, **6,** 2115 (1929).

McBain, Some Recent Advances in Colloids, **17,** 109, (1940).

Elder, Red Gold Sols, **17,** 512 (1940).

Hauser, Colloids in Your Daily Life, **18,** 590 (1941).

Morris, How Many Colloids Have You Used Today?, **3,** 438 (1926).

Bray, Aerosols—Clouds, Dust, Fog, and Smoke, **6,** 1486 (1929).

Zimmerman, The Application of Colloidal Chemistry to Foods, **3,** 1282 (1926).

Gortner, Colloids in Biochemistry, **11,** 279 (1934).

Travis, Colloids in Industry, **3,** 324 (1926).

Szymanowitz, Colloidal Graphite, Its Preparation, Properties, and Diversified Uses in Industry, **16,** 413 (1939).

Szymanowitz, An Application of Colloid Chemistry to Lubrication, **3,** 909 (1926).

CHAPTER XX

IONIC EQUILIBRIA

On the basis of a knowledge of the general characteristics of reversible reactions and chemical equilibrium (Chap. XII) together with information acquired in the study of theories of ionization (Chap. XVII), it is possible to pursue further the study of reactions of ions in solution. The ionization of weak electrolytes and numerous important kinds of metathetical reactions (Chap. XVIII) are concerned with equilibria involving ions. The study of such equilibria is particularly important in relation to their applications to problems in analytical chemistry, both qualitative and quantitative.

20.1. Ionization of Weak Electrolytes

The ionization of a solution of a weak electrolyte is represented as an equilibrium between un-ionized molecules of the solute and its ions. For example, the following equations illustrate, respectively, the ionization of a weak acid, $HC_2H_3O_2$, and a weak base, NH_4OH:

$$HC_2H_3O_2 \rightleftharpoons H^+ + (C_2H_3O_2)^-$$
$$NH_4OH \rightleftharpoons (NH_4)^+ + (OH)^-$$

In 0.1 N solution of ammonium hydroxide, the concentration of ammonium and hydroxyl ions is very low, since at this concentration NH_4OH is only 1.3 per cent ionized (Sec. 17.6). Because these two ions must be formed in equivalent amounts, the actual concentrations present in a 0.1 N solution are

$$[NH_4^+] = [OH^-] = 0.1 \times 0.013 = 0.0013\ N$$

Thus, while the solution is 0.1 N with respect to the total potential NH_4OH content of the solution, it is only 0.0013 N with respect to NH_4^+ and OH^-, owing to the slight degree of ionization. The equilibrium constant for this reaction is given by the following expression:

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = K_i$$

where K_i represents an "ionization constant" which is nothing more than the equilibrium constant for an ionization equilibrium. By sub-

stituting the actual numerical values for the three concentration terms,

$$\frac{0.0013 \times 0.0013}{1 - 0.0013} = K_i$$

and solving, the numerical value for the ionization constant is obtained:

$$\frac{(0.0013)^2}{0.0987} = K_i$$
$$0.0000171 = K_i$$
$$1.71 \times 10^{-5} = K_i$$

In effect, the concentration of un-ionized molecules of ammonium hydroxide is so large in comparison with the concentration of its ions that, for most purposes, the term $[NH_4OH]$ may be considered to be constant. By eliminating this term and considering only the concentration of the ammonium and hydroxyl ions, there obtains,

$$[NH_4^+] \times [OH^-] = K_i$$
$$.0013 \times 0.0013 = K_i$$
$$1.69 \times 10^{-6} = K_i$$

In this case, the constant is more properly referred to as the *ion product constant.* The particular numerical value given above corresponds to a 0.1 N solution of NH_4OH, and different values would be found for different concentrations of the weak electrolyte. Similar calculations may be made for acetic acid or any other weak electrolyte but not in the case of strong electrolytes that are completely ionized. In this latter case, correction would have to be made for the fact that, except at very low concentrations, the ions of strong electrolytes are not completely active (Sec. 17.4).

Common Ion Effect. Continuing to use the case of ammonium hydroxide as an example, suppose that, by adding a soluble ammonium salt such as ammonium nitrate, the concentration of ammonium ions is increased from 0.0013 N to 1.0013 N. Under these conditions, the number of ammonium ions in the solution will have been so greatly increased that hydroxyl ions will collide with ammonium ions much more frequently than in the original 0.1 N ammonium hydroxide solution. This results in the formation of more un-ionized molecules of NH_4OH, *i.e.*, the reverse reaction

$$NH_4OH \rightleftharpoons NH^+ + OH^-$$

is favored by the increase in the concentration of ammonium ions. Since the concentration of ammonium ions has been increased and because the numerical value of the ionization constant must remain

the same, it follows that the concentration of hydroxyl ions must decrease. Accordingly, let m = the fraction of the total normality of OH^- (or NH^+) consumed in the establishment of the new equilibrium mixture. The actual concentration of ammonium and hydroxyl ions remaining will be $(1.0013 - m)$ and $(0.0013 - m)$; hence,

$$(1.0013 - m) \times (0.0013 - m) = 1.69 \times 10^{-6}$$
$$m = 0.0012987\ N$$

Thus, the concentration of ammonium ions is decreased from 1.0013 N to 1.0013 − 0.0012987, or a value not much less than 1.0013 N. On the other hand, the concentration of hydroxyl ions has been decreased from 0.0013 N to 0.0013 − 0.0012987, or to 0.00000013 N, a value only one one-thousandth as great as that for the concentration of hydroxyl ions of the 0.1 N ammonium hydroxide solution before addition of ammonium nitrate.

The foregoing case illustrates a situation which is common to all weak electrolytes and which is usually referred to as the *common ion effect.* If to a solution of a weak electrolyte one adds a strong electrolyte which furnishes an ion in common with one of the products of the ionization of the weak electrolyte, a new equilibrium mixture containing more un-ionized molecules of the weak electrolyte will (owing to mass action) result. The concentration of the noncommon ion will be decreased to an extent that is dependent only upon the quantity of the common ion introduced.

Utilization of the Common Ion Effect. It is frequently possible to take advantage of the operation of the common ion effect in exercising control over the concentration of ions in solutions. Suppose that for some particular purpose one wished to use 0.1 N acetic acid but found that the concentration of hydrogen ions in the solution was too great for the purpose at hand. Since acetic acid ionizes as follows,

$$HC_2H_3O_2 \rightleftharpoons H^+ + (C_2H_3O_2)^-$$

the addition of the strong electrolyte sodium acetate would serve to increase the concentration of acetate ions. This would result in the production of a new equilibrium mixture containing more un-ionized molecules of $HC_2H_3O_2$, thus decreasing the concentration of hydrogen ions. By making suitable calculations similar to those illustrated above, one could calculate the weight of sodium acetate required to lower the concentration of hydrogen ions to any desired value.

In the systematic procedures of chemical analysis also, advantage may be taken of the operation of the common ion effect in preventing the undesirable partial precipitation of certain ions from their solutions.

This situation may be illustrated by the case of magnesium ions. If, to a solution of magnesium nitrate, or any other soluble magnesium salt one adds ammonium hydroxide solution, the concentration of hydroxyl ions supplied by the ionization of NH_4OH is sufficient to permit the occurrence of the metathetical reaction,

$$Mg^{++}(NO_3)_2^- + 2NH_4OH \rightleftharpoons \underline{Mg(OH)_2} + 2NH_4^+NO_3^-$$

A white precipitate of insoluble magnesium hydroxide appears but, under these conditions, only a part of the magnesium ions in the solution will be converted to insoluble magnesium hydroxide. Initially, the precipitation reaction proceeds rapidly but becomes progressively slower until finally equilibrium is established before the forward reaction can reach completion. The reason for this behavior lies in the fact that for every molecule of magnesium hydroxide formed there is formed also a molecule of the strong electrolyte, $NH_4^+NO_3^-$. Thus, as the formation of magnesium hydroxide proceeds, the $[NH_4^+]$ is progressively increased and this, by the common ion effect, operates to depress the ionization of ammonium hydroxide to such a point that the $[OH^-]$ becomes insufficient to permit further formation of magnesium hydroxide. In chemical analysis, *partial* precipitation of any ion is usually undesirable. Hence, it would be better to prevent entirely the precipitation of Mg^{++} as the insoluble hydroxide. This can be accomplished by adding, in advance, an ammonium salt such as ammonium nitrate. If this is done before addition of ammonium hydroxide, the $[NH_4^+]$ will be so great that the resulting $[OH^-]$ will be too small to permit formation of any insoluble magnesium hydroxide.

20.2. Hydrolysis

The term *hydrolysis* is used to describe metathetical reactions in which water is one of the reactants. Water is a very weak electrolyte which ionizes as follows:

$$H_2O \rightleftharpoons H^+ + OH^-$$

At 25°C., the concentration of hydrogen ions in pure water is 0.0000001 or 1×10^{-7} N and, since the two ions are formed always in equivalent amount, the concentration of hydroxyl ions has the same value. Hence, the ion product constant is

$$\begin{aligned} [H^+] \times [OH^-] &= K_i \\ (1 \times 10^{-7}) \times (1 \times 10^{-7}) &= K_i \\ 1 \times 10^{-14} &= K_i \end{aligned}$$

Since this value for the ion product is maintained in aqueous solutions,

any factor that changes the concentration of either of these ions will result in a corresponding change in the concentration of the other, but in an opposite direction. Thus, a water solution which is 1 N with respect to hydrogen ions must be 1×10^{-14} N with respect to hydroxyl ions since

$$\begin{aligned} [H^+] \times [OH^-] &= 1 \times 10^{-14} \\ 1 \times [OH^-] &= 1 \times 10^{-14} \\ [OH^-] &= 1 \times 10^{-14} \end{aligned}$$

Conversely, if a water solution is 1 N with respect to hydroxyl ions, it must be 10^{-14} N with respect to hydrogen ions.

When solid potassium cyanide is added to pure water, a reaction of hydrolysis ensues and the salt is said to be *hydrolyzed.*

$$K^+CN^- + HOH \rightleftharpoons K^+OH^- + HCN$$

It will be observed that this and other reactions involving hydrolysis are essentially the reverse of the corresponding neutralization reactions. Thus, in the preceding example, a salt and water react to form a strong base and a weak acid. By virtue of the occurrence of this reaction, the $[H^+]$ is decreased because hydrogen ions are bound up in the form of extremely slightly ionized molecules of hydrocyanic acid (HCN). Furthermore, the inherent slight degree of ionization of HCN is rendered still less extensive owing to a common ion effect brought about by the high $[CN^-]$ furnished by the strong electrolyte, potassium cyanide. Direct experimental measurement of the concentration of hydrogen ions in a water solution of potassium cyanide shows that $[H^+] = 1 \times 10^{-10}$ N. Since the $[H^+]$ has been decreased, the $[OH^-]$ must increase, and the numerical value of the $[OH^-]$ must be such that the ion product of water will be maintained, *i.e.*,

$$\begin{aligned} [H^+] \times [OH^-] &= 1 \times 10^{-14} \\ (1 \times 10^{-10}) \times [OH^-] &= 1 \times 10^{-14} \\ [OH^-] &= \frac{1 \times 10^{-14}}{1 \times 10^{-10}} \\ [OH^-] &= (1 \times 10^{-14}) \times (1 \times 10^{10}) \\ [OH^-] &= 1 \times 10^{-4}\ N \end{aligned}$$

When the concentration of hydroxyl ions reaches this value, the ionization of water is depressed to such an extent that further hydrolysis of the potassium cyanide cannot occur. Thus, the extent of hydrolysis of KCN is dependent upon the extent to which *un-ionized* molecules of HCN are formed.

When sodium acetate is hydrolyzed,

$$Na^+C_2H_3O_2^- + HOH \rightleftharpoons Na^+OH^- + HC_2H_3O_2$$

the actual extent to which hydrolysis will occur before equilibrium is established will be less than in the case of KCN, because $HC_2H_3O_2$ is a stronger acid than HCN and is therefore less effective in tying up the hydrogen ions provided by the ionization of water. Accordingly, in the case of sodium acetate, the $[H^+]$ is greater, and the required increase in the $[OH^-]$ (to permit maintenance of the value of 1×10^{-14} for the ion product of water) is less; hence, sodium acetate is less extensively hydrolyzed than potassium cyanide.

Hydrolysis in Relation to Types of Salts. It is apparent from the preceding examples that the occurrence and the extent of hydrolysis are related to the nature of the acid and base which might be considered as the "parents" of the particular salt. Fortunately, it is possible to consider hydrolysis in terms of such relationships.

1. *Salts of Strong Acids and Strong Bases.* Ordinarily sodium chloride might be expected to hydrolyze as follows:

$$Na^+Cl^- + HOH \rightleftharpoons Na^+OH^- + H^+Cl^-$$

However, the products Na^+OH^- and H^+Cl^- are both strong electrolytes and the ions of each are essentially equally highly active. Consequently, the occurrence of this reaction could produce nothing that would result in any unbalancing of either the $[H^+]$ or the $[OH^-]$ corresponding to that of pure water. Hence, in a water solution of sodium chloride, $[H^+] = [OH^-] = 1 \times 10^{-7}$, the ion product constant is essentially the same as that for pure water and this leads to the conclusion that there is no reason why such a salt should hydrolyze. **Salts of strong acids and strong bases are not appreciably hydrolyzed.**

2. *Salts of Strong Bases and Weak Acids.* As has already been shown in the case of potassium cyanide and sodium acetate, **salts of strong bases and weak acids hydrolyze to form basic solutions.** In any given case, the extent of hydrolysis is inversely proportional to the ionization constant of the weak acid formed in the hydrolytic reaction. In general, the weaker the acid that is formed, the greater will be the extent of hydrolysis.

3. *Salts of Weak Bases and Strong Acids.* The hydrolysis of a salt such as ammonium chloride would be expected to occur as shown by the equilibrium,

$$NH_4^+Cl^- + HOH \rightleftharpoons NH_4OH + H^+Cl^-$$

since hydroxyl ions become bound up in the formation of slightly

ionized molecules of the weak base, NH_4OH. If the $[OH^-]$ is thereby decreased, hydrolysis must continue until the $[H^+]$ is increased to such a value that the product of these two ion concentrations will be equal to 1×10^{-14}. Thus, the extent of hydrolysis of a salt of a weak base and a strong acid is inversely proportional to the ionization constant of the weak base, *i.e.*, the weaker the base that is formed in the hydrolytic reaction, the greater will be the extent of hydrolysis. **Salts of weak bases and strong acids hydrolyze to form acidic solutions.** This generalization applies equally well to bases such as $Fe(OH)_3$, $Bi(OH)_3$, and $Cu(OH)_2$, which are weak bases by virtue of the fact that they are practically insoluble in water.

4. *Salts of Weak Acids and Weak Bases.* The equation for the reaction between ammonium acetate and water,

$$NH_4^+C_2H_3O_2^- + HOH \rightleftharpoons NH_4OH + HC_2H_3O_2$$

shows that the products consist of a weak acid and a weak base, both of which are ionized to essentially the same extent. For this reason, the ionization equilibrium of water is progressively displaced to the right to provide H^+ and OH^- ions which are subsequently utilized in the formation of slightly ionized molecules of acetic acid and ammonium hydroxide. Thus, the hydrolysis proceeds far toward completion since neither a high $[H^+]$ nor $[OH^-]$ is produced to prevent further hydrolysis. Accordingly, it may be said that **salts of weak acids and weak bases are extensively hydrolyzed to form neutral, weakly basic or weakly acidic solutions, depending on the relative "strengths" of the parent acids and bases.**

20.3. Acid-base Reactions

Although the nature of acids and bases as well as neutralization reactions has already been discussed (Chap. XI and Sec. 18.5), certain aspects of acid-base reactions may be considered profitably in terms of a considerably different point of view.

Brønsted Theory. In view of the fact that pure gaseous hydrogen chloride is a predominantly covalent compound which does not possess the properties of an acid, there should be some means of explaining why a water solution of hydrogen chloride (hydrochloric acid) exhibits the properties of a solution of a strong electrolyte.

An explanation may be provided on the basis of a theory proposed by Brønsted (Fig. 87) in 1923. The characteristic feature of this theory is that it broadens one's viewpoint to the extent of including as acids and bases many substances not previously classified under these

headings. In terms of Brønsted's views, when HCl is dissolved in water the following equilibrium is established:

$$HCl + H_2O \rightleftharpoons (H_3O)^+ + Cl^-$$

The acidic properties of the solution are attributed to the ion $(H_3O)^+$, which is known as the *hydronium ion* and which is considered to be a hydrated proton, *i.e.*, $H^+ \cdot H_2O$. On this basis, the interaction of sodium hydroxide and hydrochloric acid would be represented by the equation,

$$(H_3O)^+Cl^- + Na^+(OH)^- \rightarrow 2H_2O + Na^+Cl^-$$

The ionization of other acids and their reactions with bases may be represented in a similar manner.

In the light of this point of view, an acid may be defined as any substance (molecule or ion) that is capable of furnishing or donating a hydrogen ion (*i.e.*, a proton). Thus, the HCl is considered to be an acid because it donates a proton to the water molecule in the formation of the hydronium ion. Similarly, a base is defined as any molecule or ion capable of accepting a proton. Accordingly, the water molecule should be classified as a base in these reactions since it unites with (accepts) a proton in the process of forming the hydronium ion.[1] The hydroxyl ion $(OH)^-$, the acetate ion $(C_2H_3O_2)^-$, the carbonate ion $(CO_3)^=$, and in fact any negative ion capable of uniting with hydrogen ions would also be classified as a base.

FIG. 87.—J. N. Brønsted (1879–). (*Courtesy of Professor Ralph E. Oesper University of Cincinnati.*)

Although useful in explaining many aspects of chemical behavior not otherwise readily understood, the Brønsted theory has certain

[1] Although a water molecule that accepts a proton should be classed as a base, any water molecule that furnishes a proton must be classed as an acid. Thus, in the ionization of water,

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

one water molecule acts as an acid and the other as a base (see Sec. 20.5).

serious limitations and shortcomings. For this reason, the use of these views will be limited to those few cases in which it is believed that satisfactory explanations cannot be provided on any other basis. It is significant that, although the Brønsted theory is a relatively modern development, there is at the present time considerable reason for believing that it may be superseded in the future by a still more comprehensive theory of acids, bases, and acid-base reactions.

Relative Strengths of Acids and Bases. In terms of the Brønsted theory, the relative strengths of any two acids are dependent upon their relative abilities to serve as proton donors. The ionization of hydrochloric and acetic acids may be represented by the equilibria,

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

The ionization equilibrium of HCl is shifted far toward the right while that of $HC_2H_3O_2$ is displaced to the right to only a relatively slight extent. Thus, HCl is said to be a stronger acid than $HC_2H_3O_2$ because it is a much more active proton donor.

Looking upon these same equilibria from the standpoint of the relative strengths of the bases involved, one must recognize that, in each of these cases, two bases (proton acceptors) are competing for the protons donated by the acids. Thus the two bases, H_2O and Cl^-, compete for the proton furnished by HCl and, since the equilibrium is shifted far toward the right, one must conclude that the water molecule is a stronger base than the chloride ion. Similarly, in the case of acetic acid, the acetate ion must be a stronger base than the water molecule for in this case the equilibrium is shifted far toward the left. Furthermore, it follows that the acetate ion must be a considerably stronger base than the chloride ion.

Effective Acidity versus Total Acidity. If it is admitted that hydrochloric is a stronger acid than acetic, the question at once arises as to why the same quantity of base is required to neutralize 1 mole each of these acids. The answer, of course lies in the fact that in either case the neutralization reaction involves the combination of the hydronium ion with the hydroxyl ion which is a base much stronger than Cl^-, $C_2H_3O_2^-$, or H_2O.

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

As the hydronium ions furnished by either HCl or $HC_2H_3O_2$ are thus consumed, the two ionization equilibria (see above) are shifted farther and farther toward completion until, finally, neutralization is complete in each case. Hence it must be concluded that, in comparing any two

acids that contain the same number of potential protons, the active concentration of hydronium ions may differ greatly and yet the total potential acidity will be the same.

Effective Concentration of Hydrogen Ions. Particularly where low acidities are involved, the expression of the $[H^+]$ in terms of normalities is somewhat cumbersome. Thus the $[H^+]$ in pure water is 0.0000001 N and that of a 1 N solution of sodium hydroxide is 0.00000000000001 N. Such values may, of course, be expressed somewhat more simply as 1×10^{-7} N and 1×10^{-14} N, respectively. However, since botanists, biologists, physicians, and others less accustomed to these schemes of notation frequently have need to express effective hydrogen-ion (or hydronium-ion) concentrations, it has been found desirable to adopt a still simpler scheme which has come into wide use in the various branches of chemistry also. Such a scheme is the "pH scale" or "hydrogen-ion index" devised by Sörensen (Fig. 88). In this system, the pH value of a solution is defined by

FIG. 88.—S. P. L. Sörensen (1868–1939). (*Courtesy of Professor Ralph E. Oesper, University of Cincinnati.*)

$$pH = \log \frac{1}{[H^+]}$$

Thus for pure water, $[H^+] = 1 \times 10^{-7}$ mole per liter, and the pH value is given by

$$pH = \log \frac{1}{1 \times 10^{-7}} = \log 1 \times 10^7 = 7$$

If the $[H^+]$ of a solution is known or can be determined experimentally by any one of several available methods, the pH value may be calculated as indicated above. Also, methods have been devised for the fairly accurate direct measurement of acidities in terms of pH values. The relationship between the pH scale and the corresponding acidities expressed in normalities is shown in Table 25. The pH value of the human blood is about 7.2 (*i.e.*, slightly basic) and may not vary greatly from this value without fatal results. The pH of soils is sometimes

regulated by the addition of lime. Cooking, baking, brewing, and many other operations depend upon regulated acidities usually expressed in terms of pH values.

TABLE 25
RELATION BETWEEN pH VALUES AND NORMALITY

Normality with respect to H^+...........	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
Corresponding pH values..............	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

$H^+ = 1\ N$ ← increasing acidity — neutrality — increasing basicity → $OH^- = 1\ N$

20.4. Precipitation Reactions

Many common laboratory procedures and industrial chemical operations depend upon the occurrence of reactions in solution which result in the formation of insoluble solids, or precipitates. For example, insoluble nickel sulfide is precipitated when a solution containing nickel ions is treated with a solution containing sulfide ions,

$$Ni^{++} + S^{=} \rightleftharpoons \underline{NiS}$$

The equilibrium is shifted very far toward the right, so that for many purposes the reaction may be considered as having proceeded to completion. However, this or any similar reaction does not proceed *entirely* to the right and, as a result, when precipitation has been rendered as complete as possible, some nickel ions and sulfide ions remain in the solution where they exist in equilibrium with the precipitated nickel sulfide (Fig. 89). The concentration of the ions remaining in the solution (*i.e.*, not precipitated) is related to the solubility of the precipitate under consideration.

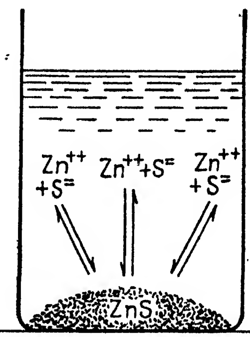


FIG. 89.—A precipitate in equilibrium with a solution of its ions.

Solubility Product. When, as indicated above, a solid (precipitate) is in equilibrium with a saturated solution of the corresponding ions, the product of the molar concentration of these ions is called the *solubility product.* For nickel sulfide, accurate analysis of a saturated solution of this compound shows that the solution contains 1×10^{-12}

mole of Ni^{++} per liter and, since there must be one $S^{=}$ for each Ni^{++}, the molar concentration of $S^{=}$ must have the same value. Accordingly the solubility product of nickel sulfide,

$$[Ni^{++}] \times [S^{=}] = K_{s.p.}$$

is given by

$$(1 \times 10^{-12}) \times (1 \times 10^{-12}) = K_{s.p.}$$
$$1 \times 10^{-24} = K_{s.p.}$$

The symbol, $K_{s.p.}$, is used to designate the ion product constant (equilibrium constant) which, in cases of this sort, is called the *solubility product constant.* These constant values for the ion products of saturated solutions are realized only in the case of slightly soluble substances. A low value for $K_{s.p.}$ means low solubility, which in turn implies relatively complete precipitation. For example, the $K_{s.p.}$ for CuS is 1×10^{-46}, or a value much lower than that for NiS. Consequently, under the same experimental conditions of sulfide ion concentration, Cu^{++} may be precipitated much more nearly completely than Ni^{++}. A tabulation of $K_{s.p.}$ values for various substances is given in the Appendix.

Accomplishment of Complete Precipitation. When a solution containing $S^{=}$ is added slowly to a solution containing Cu^{++}, for example, precipitation will not begin until the product of the molar concentration of Cu^{++} and $S^{=}$ is sufficient to exceed the solubility product of CuS. Once the solubility product has been exceeded, the degree to which precipitation will proceed toward completion is dependent upon the *extent* to which the $K_{s.p.}$ value is exceeded. If it is desired to precipitate Cu^{++} as nearly completely as possible,

$$Cu^{++} + S^{=} \rightleftarrows \underline{CuS}$$

a large excess of $S^{=}$ should be added. Under these conditions, the ion product

$$[Cu^{++}] \times [S^{=}] = K_{s.p.} = 1 \times 10^{-46}$$

can be maintained at 1×10^{-46} while, as the $[S^{=}]$ is progressively increased, the $[Cu^{++}]$ may be progressively decreased to a minimum. It is for this reason that an excess of the precipitating reagent is usually added.

The $K_{s.p.}$ for MnS is 1×10^{-15}. If to a solution in which the molar concentration of Mn^{++} is 1×10^{-1}, there is added a saturated aqueous solution of hydrosulfuric acid which is 0.1 N with respect to H^+, pre-

cipitation of managous sulfide will not occur. Owing to the effect of the common ion H^+, the $[S^=] = 1 \times 10^{-22}$; hence,

$$[Mn^{++}] \times [S^=] = (1 \times 10^{-1}) \times (1 \times 10^{-22}) = 1 \times 10^{-23}$$

an ion product less than the $K_{s.p.}$ for manganous sulfide. Accordingly, too small a $[S^=]$ has been provided to exceed the $K_{s.p.}$ If, however, one should add a 1×10^{-1} molar solution of the strong electrolyte, $(NH_4)_2^+ S^=$, then

$$[Mn^{++}] \times [S^=] = (1 \times 10^{-1}) \times (1 \times 10^{-1}) = 1 \times 10^{-2}$$

or an ion product much greater than 1×10^{-15}. Under these conditions, precipitation of manganous sulfide will occur and since 1×10^{-2} is so much greater than 1×10^{-15}, the precipitation reaction will proceed essentially to completion.

20.5. Amphoteric Hydroxides

Just as is true of the precipitation of sulfides, so the precipitation of hydroxides may often be forced toward completion by the addition of an excess of the precipitating reagent.

$$Bi^{+++}(NO_3)_3^- + \underset{\text{(excess)}}{3Na^+OH^-} \rightleftharpoons \underline{Bi(OH)_3} + 3Na^+NO_3^-$$

In a few cases, however, a quite different result is realized. The hydroxides of zinc, tin, lead, and aluminum are *redissolved* when an excess of the precipitating reagent (Na^+OH^-) is added; thus,

$$Zn^{++}(NO_3)_2^- + 2Na^+OH^- \rightleftharpoons \underline{Zn(OH)_2} + 2Na^+NO_3^-$$
$$\underline{Zn(OH)_2} + Na^+OH^- \rightarrow H_2O + Na^+HZnO_2^-$$

The products of the second reaction are water and sodium hydrogen zincate [the acid salt of zincic acid (H_2ZnO_2)] and since sodium hydroxide is a strong base, zinc hydroxide must (in this reaction) behave as an acid, for which the formula should be changed from $Zn(OH)_2$ to H_2ZnO_2. The equation then becomes

$$H_2ZnO_2 + Na^+OH^- \rightarrow H_2O + Na^+HZnO_2^-$$

Of course, zinc hydroxide and sodium hydroxide are both bases, but in the presence of the strong base Na^+OH^-, the weak base $Zn(OH)_2$ behaves as an acid. If, on the other hand, the weak base $Zn(OH)_2$ is brought into the presence of an acid that is stronger than H_2ZnO_2, the zinc hydroxide behaves as a base.

$$Zn(OH)_2 + 2H^+Cl^- \rightarrow 2H_2O + Zn^{++}Cl_2^-$$

Hydroxides that exhibit this dual behavior of functioning either as an acid or a base are called *amphoteric hydroxides*, and the ionization equilibria may be represented as follows:

In the presence of a strong acid:

$$\underline{Zn(OH)_2} \rightleftharpoons Zn^{++} + 2OH^-$$

In the presence of a strong base:

$$\underline{H_2ZnO_2} \rightleftharpoons H^+ + HZnO_2^-$$
$$HZnO_2^- \rightleftharpoons H^+ + ZnO_2^=$$

Similar behaviors are exhibited by $Sn(OH)_2$ and $Pb(OH)_2$. The case of $Al(OH)_3$ is different to the extent that an intermediate dehydration reaction takes place.

$$Al^{+++}(NO_3)_3^- + 3Na^+OH^- \rightarrow \underline{Al(OH)_3} + 3Na^+NO_3^-$$
$$\underline{Al(OH)_3} \rightarrow H_2O + \underline{Al(O)OH}$$
$$H^+AlO_2^- + Na^+OH^- \rightarrow H_2O + Na^+AlO_2^-$$

In any event, the role that is assumed by an amphoteric hydroxide is dependent upon the environment into which it is placed.

20.6. Complex Ions

In certain cases, the precipitation of insoluble hydroxides is also accomplished by the use of ammonium hydroxide, *e.g.*,

$$Al^{+++}Cl_3^- + 3NH_4OH \rightarrow \underline{Al(OH)_3} + 3NH_4^+Cl^-$$

which furnishes a $[OH^-]$ which is very low but which is nevertheless great enough to exceed the very low $K_{s.p.}$ values for a few hydroxides, such as those of aluminum, iron, and bismuth. In these few cases, the precipitation reactions proceed essentially to completion because of the low solubility (low $K_{s.p.}$ value) of these hydroxides and in spite of the common ion effect occasioned by the concurrent establishment of an increased concentration of ammonium ions.

The reagent commonly called *ammonium hydroxide* is produced by dissolving gaseous ammonia in water. In the resulting solution, the following equilibria are established:

$$NH_{3(\text{dissolved})} + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Both of these equilibria are shifted far toward the *left*, hence, most of the NH_3 in the solution is present simply as dissolved molecules of ammonia. Since NH_4OH molecules are formed only to a slight extent and since these, in turn, ionize only to a very limited degree, it is appar-

ent why ammonium hydroxide provides only a very low concentration of hydroxyl ions.

Owing to the presence of dissolved ammonia, some soluble salts react preferentially with ammonia molecules rather than with the available hydroxyl ions; thus,

$$Ag^+NO_3^- + 2NH_3 \rightarrow [Ag(NH_3)_2]^+NO_3^-$$

Similarly, insoluble silver chloride is dissolved upon addition of ammonium hydroxide.

$$\underline{AgCl} + 2NH_3 \rightarrow [Ag(NH_3)_2]^+Cl^-$$

The salts, $[Ag(NH_3)_2]^+NO_3^-$ and $[Ag(NH_3)_2]^+Cl^-$, are examples of a class of compounds known as *metal ammines* and serve as examples of salts involving *complex ions*. Other examples of metal ammines are $[Cu(NH_3)_4]^{++}SO_4^=$, $[Cd(NH_3)_4]^{++}Cl_2^-$, $[Zn(NH_3)_4]^{++}(NO_3)_2^-$, and $[Ni(NH_3)_4]^{++}Br_2^-$.

Very commonly (but not always) the number of molecules of ammonia in combination with the metal ion is twice the valence of the metal ion.

In complex ions such as $[Ag(NH_3)_2]^+$ and $[Cd(NH_3)_4]^{++}$, the ammonia molecules are relatively loosely bound to the metal ion by a type of valence that will not be considered here in detail. Usually, such complex ions involving ammonia molecules may be destroyed by the addition of a strong acid, *e.g.*,

$$[Ag(NH_3)_2]^+Cl^- + 2H^+NO_3^- \rightarrow \underline{Ag^+Cl^-} + 2NH_4^+NO_3^-$$

Numerous examples of the formation of complex ions will be encountered by the student, particularly in connection with laboratory work. For that matter, the hydronium ion, H_3O^+, may be so considered, thus $[H(H_2O)]^+$. Similarly, a water solution of aluminum chloride is known to contain complex ions of the formula $[Al(H_2O)_6]^{+++}$.

EXERCISES

1. Distinguish between the following groups of terms: (*a*) equilibrium constant, ion product constant, and solubility product constant; (*b*) hydrolysis and neutralization, (*c*) total acidity and effective concentration of hydrogen ions.

2. Why is the ionization of strong electrolytes not represented as an equilibrium as in the case of weak electrolytes?

3. How is the common ion effect related to the law of mass action?

4. What determines the *extent* to which a salt will undergo hydrolysis?

5. List four classes of salts, and indicate (*a*) whether each will be hydrolyzed upon contact with water and (*b*) the nature of the resulting solution in each case.

6. In terms of the Brønsted theory, show that water may be looked upon either as an acid or a base.

7. Would it be proper to classify water as an amphoteric hydroxide? Why?

8. Two solutions are prepared so that one contains 36.457 g. of HCl and the other 97 g. of HSO_4^-. How do these two solutions compare as to (*a*) effective $[H^+]$ and (*b*) total available acidity?

9. How would the $[OH^-]$ in an aqueous solution of ammonia be influenced by an elevation of the temperature?

10. If a 0.1 molar solution of copper nitrate is rendered 0.1 N with respect to H^+ and thereafter saturated with hydrogen sulfide gas, show that the $K_{s.p.}$ of copper sulfide will be exceeded.

11. When two solutions containing solutes that react to form a sparingly soluble substance are brought together, what requirement must be met if the insoluble substance is to appear as a precipitate?

12. Suggest an alternative formula for the hydrate, $CuSO_4 \cdot 5H_2O$.

13. Which of the following solutions will provide the greater $[Hg^{++}]$: (*a*) a 0.1 molar solution of mercuric chloride or (*b*) a 0.1 molar solution of mercuric chloride containing some dissolved sodium chloride?

14. What analogy exists between amphoteric hydroxides and amphoteric elements?

SUGGESTED READING

Journal of Chemical Education

Dow, The Equilibrium Constant Equation, **17**, 439 (1940).

O'Brien and Kenny, The Hydrolysis of a Salt Derived from a Weak Acid and Weak Base, **16**, 140 (1939).

Foster, Why Not Modernize the Textbooks Also? II. Hydrolysis and Its Relation to Ionic Charge and Radius, **17**, 509 (1940).

Kilpatrick, Acids, Bases, and Salts, **12**, 109 (1935).

Hazlehurst, Acid-base Reactions, **17**, 466 (1940).

Hazlehurst, Pictures of Acid-base Reactions, **17**, 374 (1940).

Alyea, A Résumé of the Proton Transfer Concept of Acids and Bases, **18**, 206 (1941).

Ginell, Acids and Bases; A Critical Reevaluation, **20**, 250 (1943).

Ashley, Hydrogen Ion Concentration, **5**, 1647 (1928).

Kilpatrick and Kilpatrick, The Definition of pH, **9**, 1010 (1932).

Gorman, A Review of the Interpretation of pH, **17**, 343 (1940).

French, pH Determinations in Elementary Chemistry, **13**, 534 (1936).

Taylor, The Application of pH Control, **6**, 36 (1929).

Denbigh, The Theory of Solubility Product, **18**, 126 (1941).

Zuffanti, Solubility Product, **17**, 433 (1940).

Josten, A Geometric Means of Teaching Solubility Product, **17**, 345 (1940).

Seward, Reactions of Metallic Hydroxides with Bases, **11**, 567 (1934).

CHAPTER XXI

ELECTROLYSIS

The use of electrical conductance as an aid in determining whether certain solutes should be classified as electrolytes or nonelectrolytes (Sec. 17.2) together with references to the use of electricity in the decomposition of certain compounds (Sec. 8.5) suggests that electrical energy often may be used to advantage in chemistry. In fact, it may be stated that both in the laboratory and in the chemical industries, electricity is one of the most important tools that the chemist has at his command. Following a study of the nature of the chemical changes that may be brought about through the agency of electrical energy, numerous important commercial applications will be considered in some detail.

21.1. Electrolytic Cells

The process of **electrolysis may be defined as the transformation of chemical substances as the result of passage of the direct**

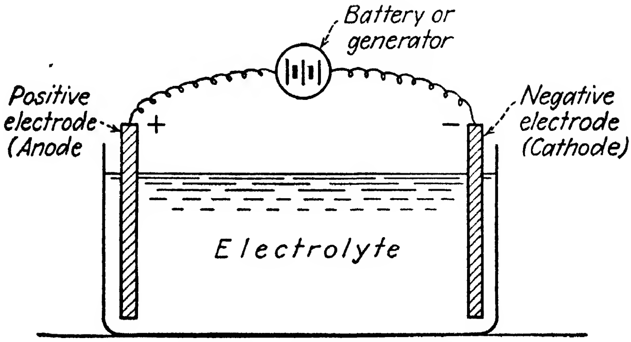


FIG. 90.—Electrolytic cell.

electric current. In order to bring about such transformations, the use of certain more or less highly specialized apparatus is necessary or at least convenient. A simple form of electrolytic cell is illustrated by Fig. 90. The cell as a whole consists of a vessel containing a solution of an electrolyte in which are immersed two electrodes (or poles). The electrodes are connected to storage batteries or to a generator which serve as sources of the electrical energy needed to bring about the

desired electrolytic transformation. The electrode through which the flow of electrons enters the cell is known as the *cathode* and is designated as the *negative* (−) electrode. By convention, the other electrode which is called the *anode* may be thought of as that through which electrons are withdrawn from the solution and this electrode is designated as *positive* (+). Throughout the following sections, the terms *cathode* and *anode* will be used to designate the negative and positive electrodes, respectively.

It must be recognized that Fig. 90 is only a highly simplified representation of an electrolytic cell. Actual commercial practice usually employs a connected series of such cells constructed in such manner as to meet the needs of each specific operation. Frequently the vessel containing the electrolyte is made of metal and serves as one of the electrodes. Other modifications will be shown in connection with commercial applications of electrolysis.

21.2. Electrolysis of Zinc Chloride Solution

The occurrence of a simple electrolysis may be demonstrated conveniently by passing a direct current through an aqueous solution of zinc chloride. A rectangular glass vessel (Fig. 91) is filled partly with

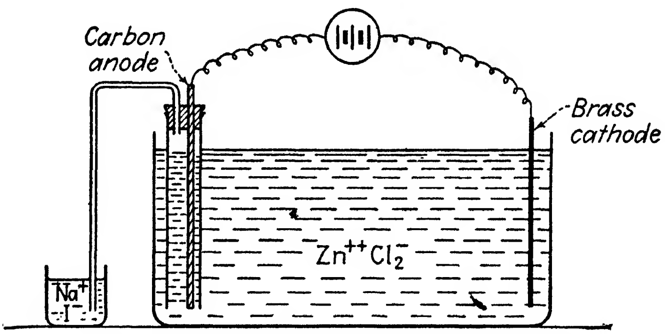


FIG. 91.—Electrolysis of zinc chloride solution.

zinc chloride solution. A polished strip of brass serves as the cathode while a carbon rod constitutes the anode. In this particular case, the use of a carbon rod rather than a metal is advisable since most metals would react chemically with one of the products of the electrolysis, thus complicating the situation with secondary reactions not concerned with the primary process of electrolysis. Further, it is convenient to surround the anode with a glass housing in which the gaseous electrolysis product may be collected and from which it may be continuously withdrawn through a suitable exit tube.

Immediately upon connecting the cell to a source of direct current,

a deposit of gray metallic zinc appears on the surface of the cathode and bubbles of chlorine gas appear at the surface of the anode. A simple chemical test for chlorine may be made by leading this gas into aqueous sodium iodide solution, whereupon the solution assumes a yellow color caused by displacement of iodine by chlorine (Sec. 13.5). Accordingly, it is concluded that the products of the electrolysis of zinc chloride solution are elemental zinc and elemental chlorine, and the next problem is that of explaining by what mechanism these products may be produced.

The solution in the cell contains zinc ions (Zn^{++}) and chloride ions (Cl^-). The chloride ions are attracted to the anode (+ electrode) where they give up electrons and form molecules of elemental chlorine.

$$\text{At anode: } 2Cl^- - 2e^- \rightarrow \overline{Cl}{}_2^0$$

The battery acts as a "pump" and forces these electrons through the outside circuit and into the cathode, at the surface of which these electrons are acquired by the zinc ions in the solution surrounding the cathode, *i.e.*,

$$\text{At cathode: } Zn^{++} + 2e^- \rightarrow \underline{Zn^0}$$

Obviously, these reactions involve loss and gain of electrons and therefore are to be recognized as oxidation-reduction reactions (Sec. 18.1). The sum of the changes that occur in the regions of the anode and cathode serves to represent the over-all chemical change that occurs in the cell as a whole, *i.e.*,

$$\begin{array}{rl} \text{Anode:} & 2Cl^- - 2e^- \rightarrow Cl_2^0 \\ \text{Cathode:} & Zn^{++} + 2e^- \rightarrow Zn^0 \\ \hline \text{Cell:} & Zn^{++}Cl_2^- \rightarrow \underline{Zn^0} + \overline{Cl}{}_2^0 \end{array}$$

In order to avoid confusion, equations representing electrolysis should always be labeled as indicated above.

21.3. Some Broad Aspects of Electrolysis

The electrolysis of aqueous zinc chloride solution serves as a suitable basis for the consideration of a number of features common to all situations of this general type. These will be enumerated in terms of summarizing statements followed by some necessary explanatory remarks and illustrations.

1. **The occurrence of electrolysis requires the utilization of an outside source of electrical energy.** The chemical changes that occur during electrolysis involve an accompanying transformation of electrical energy into chemical energy. The work done during elec-

trolysis may be looked upon as that required to transfer electrons from the anode through the wires that constitute the outside electrical circuit and finally into the cathode. The magnitude of the outside energy supply required is dependent upon the particular material it is desired to electrolyze and is different for different electrolytes.

2. **The chemical changes that occur during electrolysis are forced and not spontaneous.** Depending upon their particular structures, the atoms of each kind of element exhibit a tendency either to gain or lose electrons (Sec. 15.5). Thus, chlorine atoms tend to gain electrons and become chloride ions, while zinc atoms tend to lose electrons and become zinc ions. However, as has already been shown, the electrolysis of zinc chloride solution produces exactly the reverse of these changes. Once a compound has been formed by virtue of natural tendencies of the character referred to above, the ease with which the compounds may be decomposed by electrolysis is dependent upon the magnitude of the tendencies that were responsible for the initial compound formation.

3. **The quantities of matter transformed at the two electrodes are chemically equivalent.** In other words, the quantity of chlorine gas evolved during the electrolysis of a zinc chloride solution must be exactly that quantity which would combine with the zinc deposited on the cathode to form zinc chloride. In terms of the electrons involved, the number of electrons lost at the anode must be identical with the number gained at the cathode. This requirement also follows from the fact that these reactions are oxidation-reduction changes. Although it is true that one may represent the anode and cathode reactions by what may appear to be independent chemical equations, it must always be borne in mind that a reaction may not occur at one electrode without the simultaneous occurrence of another reaction at the other electrode.

In this connection, it should also be recognized that the total quantity of matter transformed during electrolysis is proportional to the quantity of electrical energy supplied from the battery or generator. Thus, the total weight of zinc deposited upon the cathode when one electrolyzes a zinc chloride solution is related quantitatively to the total quantity of electricity supplied from without the cell.

4. **The passage of the current through the solution involves the transport of ions.** If one should construct an electrolytic cell consisting of every essential part except the electrolytic solution between the electrodes, the electrical circuit would be incomplete and current could not flow. If one now places a solution of an electrolyte between the two electrodes, the circuit is thereby completed and the

current flows through the entire circuit. Since the solution is a conductor of the second class, which may act as a conductor of electricity if transformations of matter occur, the process by which the current passes through the solution must be fundamentally different from that involved in the flow of electrons through the connecting metal wires and through the electrodes. In order to clarify this problem, it is helpful to attempt to form a mental picture as to what occurs in the solution during electrolysis of zinc chloride.

Consider first the changes that occur in the region of the cathode. Zinc ions gain electrons and are deposited in the form of metallic zinc on the surface of the cathode. Since positive ions are thus removed, the solution immediately surrounding the cathode might contain, momentarily, an excess of negative ions. However, the electrical neutrality of the solution is maintained by the migration of zinc ions from the solution farther from the cathode. At the same time, chloride ions are removed in the region of the anode and leave an excess of positive zinc ions; this causes the chloride ions in the remainder of the solution to migrate toward the anode. Thus, as electrolysis proceeds, positive ions are transported toward the cathode while at the same time negative ions are transported toward the anode, and the entire solution becomes progressively more dilute with respect to the ions involved in the reactions that occur at the two electrodes. It is this shifting or transporting of ions that is commonly referred to as the "passage of the current through the solution."

Relative Speed of Ions. The motion of cations and anions in opposite directions through the solution between the electrodes is analogous to the drawing together of two boats by means of a rope between them. Assuming that the applied pull is the same at both ends of the rope, it is evident that both boats will move at different speeds if they differ in weight. Similarly, ions that differ greatly in size do not move at the same speed. For example, during the electrolysis of hydrochloric acid solution, the very small hydrogen ions move about five times as fast as the larger chloride ions. Accordingly, five-sixths of the ability of hydrochloric acid solution to act as a conductor of electricity is attributed to the hydrogen ions and one-sixth to the chloride ions.

21.4. Faraday's Laws of Electrolysis

It has already been pointed out that the quantities of chemical changes occurring at the anode and cathode must be chemically equivalent. However, nothing really definite has been indicated with regard to the relationship between the quantities of chemical change and the quantity of electricity that flows through the cell. This rela-

tionship was established as a result of investigations carried out more than one hundred years ago by the English scientist, Michael Faraday (Fig. 92). By carefully controlled experiments, Faraday was able to prove that the extent to which chemical changes occur during electrolysis is independent of concentration, temperature, and rate of flow of the current, and dependent *only* upon the quantity of electricity that flows. The results of these studies may be summarized in generalizations which have come to be known as *Faraday's laws.*

1. **The quantity of chemical change that occurs at the electrodes during electrolysis is directly proportional to the quantity of electricity that flows through the cell.**

FIG. 92.—Michael Faraday (1791–1867).

The unit of measurement of quantities of electricity is the *coulomb,* which is that quantity required to deposit (on a cathode) exactly 0.001118 g. of silver. Since the atomic weight of silver is 107.88, the number of coulombs required to deposit 1 gram-atomic weight of silver is

$$107.88 \div 0.001118 = 96{,}500 \text{ coulombs.}$$

This number of coulombs is called *one faraday* and represents the quantity of electricity involved in the chemical transformation of 1 gram-atomic weight of *any* element having a valence of *one.* The relation between the faraday and the quantities of divalent, tervalent, etc., elements deposited is embodied in Faraday's second law.

2. **The quantities of the various elements liberated at the electrodes during electrolysis are in the ratio of their equivalent weights.** Thus, if a given quantity of electricity, 96,500 coulombs for example, is passed successively through solutions of $Ag^+NO_3^-$, $Cu^{++}(NO_3)_2^-$, and $Bi^{+++}(NO_3)_3^-$ (Fig. 93), there will be deposited from the first solution 107.88 g. of silver or 1 gram-equivalent weight. In the case of the second solution, one-half of 1 gram-atomic weight of copper, *i.e.*, 63.57/2 g., or 1 gram-equivalent weight of copper will be deposited. Similarly, one third of 1 gram-atomic weight of bismuth, 209/3 g., will be deposited. If one should electrolyze separate solutions containing chloride ions and sulfide ions by using 1 faraday of electricity, the quantities of these nonmetals liberated would be

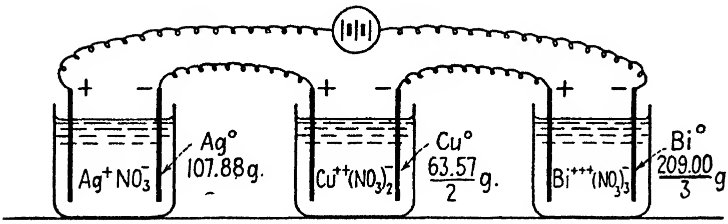


FIG. 93.—The quantities of metals deposited upon passage of 1 faraday of electricity.

35.457 g. of chlorine and 16 g. of sulfur. From these examples, it should be apparent that 1 gram-equivalent weight of an element is equal to the gram-atomic weight divided by the valence of the element.

21.5. Discharge of Ions from Aqueous Solutions

During the electrolysis of a solution of zinc chloride, both of the ions of the *solute*, *i.e.*, Zn^{++} and Cl^-, have their ionic charges neutralized at the cathode and anode, respectively. These ions may therefore be said to have been *discharged* and liberated in the form of elemental zinc and chlorine. In order to determine whether the ions corresponding to the solute are always discharged at the electrodes during electrolysis, it becomes necessary to inquire into the behavior of other electrolytes.

Electrolysis of Water. When a direct current is passed through a dilute solution of sulfuric acid, the products liberated at the electrodes are the same as would result from the electrolysis of water alone. The advantage in using dilute sulfuric acid solution rather than pure water lies in the fact that one may thus avoid the high resistance (to passage of the current) offered by the weak electrolyte, water. The products of electrolysis consist of hydrogen liberated at the cathode and oxygen liberated at the anode. If this electrolysis is carried out in a cell of the

type illustrated by the Hoffman apparatus (Fig. 94), it may be observed readily that hydrogen and oxygen are produced in a 2:1 volume ration. These products result from the discharge of hydrogen and hydroxyl ions and the reactions involved are represented by the following equations:

$$\begin{aligned} \text{Anode: } & 4OH^- - 4e^- \rightarrow O_2^0 + 2H_2O \\ \text{Cathode: } & 4H^+ + 4e^- \rightarrow 2H_2^0 \\ \hline \text{Cell: } & 4H_2O \rightarrow 2\overline{H}_2^0 + \overline{O}_2^0 + 2H_2O \end{aligned}$$

or

$$2H_2O \rightarrow 2\overline{H}_2^3 + \overline{O}_2^0$$

The dilute acid solution contained hydrogen ions supplied by the solute and also by the slight ionization of water. Particular attention should be directed at the fact that the solution contained two anions, *i.e.*, a very low concentration of hydroxyl ions and a relatively high concentration of sulfate ions. Despite the fact that the sulfate ions were present at much greater concentration than the hydroxyl ions, only the latter were discharged at the anode. From this fact alone, it may be concluded that not all anions are discharged upon electrolysis of aqueous solutions and that, in such cases, the anion of the solvent will be involved in the reaction at the anode.

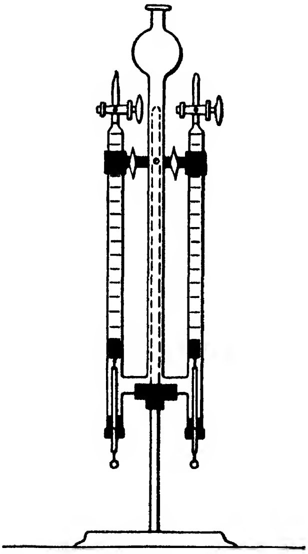


FIG. 94.—The Hoffman electrolysis apparatus.

Electrolysis of Sodium Bromide Solution. When an aqueous solution of sodium bromide is electrolyzed, hydrogen gas is liberated at the cathode and bromine gas at the anode. These products are to be anticipated because of the marked chemical similarity of bromine and chlorine (Sec. 13.5) and because sodium, even if it were liberated by the discharge of sodium ions, would react immediately with water to liberate hydrogen (Sec. 8.1). In effect, then, the electrolysis of an aqueous solution of sodium bromide involves the discharge of the anion of the solute and the cation of the solvent.

$$\begin{aligned} \text{Anode: } & 2Br^- - 2e^- \rightarrow Br_2^\circ \\ \text{Cathode: } & 2H^+ + 2e^- \rightarrow H_2^\circ \\ \hline \text{Cell: } & 2H^+ + 2Br^- \rightarrow \overline{H}_2^\circ + \overline{Br}_2^\circ \end{aligned}$$

In view of these results, one may recognize that not all cations are

discharged during the electrolysis of aqueous solutions and that the cation of the solvent may be discharged at the cathode in place of the cation of the solute.

Generalizations concerning the Discharge of Anions and Cations from Aqueous Solutions. From the foregoing cases taken together with the results of many similar experiments, it becomes possible to generalize broadly with respect to the behavior of anions and cations during the passage of the direct current through aqueous solutions of electrolytes. These general rules may be formulated as follows:

1. **All common cations may be discharged except Mg^{++}, Al^{+++}, the ions of the alkali metals, Li^+, Na^+, K^+, Rb^+, Cs^+, and those of the alkaline earth metals, Ca^{++}, Sr^{++}, and Ba^{++}.**

2. **The only common anions that may be discharged are Cl^-, Br^-, I^-, OH^-, and $S^=$.**

Thus, in the manner characteristic of an experimental science, extensive experimentation leads to generalizations that may be used thereafter in the prediction of the behavior of substances not previously investigated. Numerous examples of the utility of these general rules will be cited in the remainder of this and in subsequent chapters.

The presence of a nondischargeable anion or cation has an important bearing upon the nature of the solution remaining in the cell following the occurrence of electrolysis. In the electrolysis of sodium bromide solution, for example, the discharge of hydrogen ions (from water) occurs in the region surrounding the cathode; hence, the solution becomes basic since it contains the ions corresponding to the strong base, Na^+OH^-. Conversely, the electrolysis of an aqueous solution of copper nitrate solution would result in the formation of an acidic solution in the region of the anode since OH^- would be discharged, leaving the nondischargeable NO_3^- ions and the H^+ ions (from water). These two typical examples are in conformity with two additional generalizations which may be stated as follows:

3. **The electrolysis of an aqueous solution containing a nondischargeable cation produces a basic solution in the region of the cathode.**

4. **The electrolysis of an aqueous solution containing a nondischargeable anion produces an acidic solution in the region of the anode.**

21.6. Electrolysis of Aqueous Solutions of Salts

On the basis of the preceding generalizations, it is possible to predict the products of electrolysis of aqueous solutions of simple salts.

It is not possible, however, to predict the specific experimental conditions under which these electrolyses may be carried out most advantageously. Usually the optimum experimental conditions can be ascertained only by means of experiments relating to any particular case.

Suppose that it is desired to know what products would result from the electrolysis of an aqueous solution of nickel acetate. Referring to the general rules set forth in Sec. 21.5, it is seen that nickel ions will be discharged at the cathode and that hydroxyl ions, and not the acetate ions, will be discharged at the anode.

$$\begin{array}{rl} \text{Anode:} & 4OH^- - 4e^- \rightarrow O_2^0 + 2H_2O \\ \text{Cathode:} & 2Ni^{++} + 4e^- \rightarrow 2Ni^0 \\ \hline \text{Cell:} & 2Ni^{++} + 4OH^- \rightarrow \underline{2Ni^0} + \overline{O_2^0} + 2H_2O \end{array}$$

Furthermore, it is also apparent that the region of the anode would become progressively more acidic, owing to an accumulation of acetic acid, as the electrolysis proceeds.

In a similar manner, one would predict that the electrolysis of strontium nitrate solution will lead to the formation of oxygen gas and hydrogen gas at the anode and cathode, respectively.

$$\begin{array}{rl} \text{Anode:} & 4OH^- - 4e^- \rightarrow O_2^0 + 2H_2O \\ \text{Cathode:} & 4H^+ + 4e^- \rightarrow 2H_2^0 \\ \hline \text{Cell:} & 4H_2O \rightarrow 2\overline{H_2^0} + \overline{O_2^0} + 2H_2O \end{array}$$

or

$$2H_2O \rightarrow 2\overline{H_2^0} + \overline{O_2^0}$$

The products are the same as those resulting from the electrolysis of water since neither the cation or anion of the solute is dischargeable. During the course of this electrolysis, the region of the anode becomes acidic ($H^+NO_3^-$) and the region of the cathode becomes basic [$Sr^{++}(OH)_2^-$].

Similar predictions may be made readily with regard to the electrolysis of aqueous solutions of other salts.

21.7. Electrolysis of Aqueous Solutions of Acids

Since all soluble acids furnish hydrogen ions, it is immediately apparent that the electrolysis of aqueous solutions of acids will yield hydrogen gas at the cathode. Consequently, the only question that remains is concerned with whether the anion of the particular acid is dischargeable. If not, oxygen gas will be liberated. The two possible types of behavior are illustrated by hydriodic acid,

$$\begin{array}{rl} \text{Anode:} & 2I^- - 2e^- \rightarrow I_2^0 \\ \text{Cathode:} & 2H^+ + 2e^- \rightarrow H_2^0 \\ \hline \text{Cell:} & 2H^+I^- \rightarrow \overline{H}_2^0 + I_2^0 \end{array}$$

and phosphoric acid,

$$\begin{array}{rl} \text{Anode:} & 4OH^- - 4e^- \rightarrow O_2^0 + 2H_2O \\ \text{Cathode:} & 4H^+ + 4e^- \rightarrow 2H_2^0 \\ \hline \text{Cell:} & 4H_2O \rightarrow 2\overline{H}_2^0 + \dot{O}_2^0 + 2H_2O \end{array}$$

or

$$2H_2O \rightarrow 2\overline{H}_2^0 + \overline{O}_2^0$$

21.8. Electrolysis of Aqueous Solutions of Bases

The soluble bases are very limited in number (Sec. 18.10) and involve nondischargeable cations. Accordingly, when an aqueous solution of a base is electrolyzed, hydrogen gas is evolved at the cathode and, of course, the discharge of hydroxyl ions at the anode results in the liberations of gaseous oxygen. In such cases, the products are the same as those obtained by the electrolysis of water. Since a commercial application of the electrolysis of the strong base, sodium hydroxide, is to be described in the next chapter no further discussion of this topic seems necessary at this juncture.

21.9. Electrolysis of Fused Salts

Although many important commercial processes involve the electrolysis of aqueous solutions, this fact should by no means be interpreted as implying that one is restricted to the use of aqueous solutions. Electrolyses may be effected by employing solvents other than water (*i.e.*, *nonaqueous* solvents) or in the absence of any solvent. In any event, it is obvious that if one wished to produce a metal such as sodium, the electrolysis would have to be carried out in the absence of water. This may often be accomplished by the use of fused salts. Since most solid salt crystals consist of ions (Sec. 15.6), application of heat sufficient to melt the salt results in the formation of a molten liquid which still contains ions and is therefore capable of behaving as an electrolyte. Because of their comparatively low melting temperatures chlorides (and less frequently, hydroxides) are commonly employed. The high temperatures required to melt inorganic salts are disadvantageous and, wherever possible, a second salt is added for the purpose of lowering the melting temperature of the salt that it is desired to electrolyze. Thus, the melting temperature of sodium chloride is lowered by the addition of a relatively small quantity of barium chloride. This lowering of the melting temperature may be looked upon as being analogous to the lowering of the freezing tem-

perature of a pure solvent by the addition of a nonvolatile solute, and the added salt is usually referred to as a *flux*.

Electrolyses involving fused salts are more difficult to carry out than those in which aqueous solutions are used. The high temperatures required and the generally reactive character of the products necessitate elaborate equipment especially designed to fulfill the specific requirements in any given case. A number of typical cases in which fused salts are employed will be considered in the next chapter.

EXERCISES

1. Define the following terms: (*a*) electrolysis, (*b*) anode, (*c*) cathode, (*d*) electrode, (*e*) coulomb, (*f*) faraday, (*g*) gram-equivalent weight of an element, (*h*) flux.

2. What is the function of the battery or generator used in electrolyses?

3. With respect to the external electrical circuit, what is the direction of flow of electrons?

4. By what sort of mechanism does the current flow through the solution between the electrodes?

5. Using a suitable example other than the case of zinc chloride, show that the reactions that occur during electrolysis are not spontaneous chemical changes.

6. What similarity exists between the speed of ions in solution and the speed of motion of gas molecules?

7. State Faraday's laws of electrolysis.

8. What weight of each of the following elements may be liberated at the electrodes during the passage of 1 faraday: (*a*) zinc, (*b*) hydrogen, (*c*) chromium, (*d*) bromine, (*e*) potassium?

9. During the electrolysis of a sulfuric acid solution, 0.6439 g. of oxygen was liberated at the anode. Calculate (*a*) the number of coulombs and (*b*) the number of faradays of electricity that flowed through the cell.

10. Under what conditions and in the neighborhood of which electrode may each of the following be formed during electrolysis of aqueous solutions: (*a*) an acid, (*b*) a base?

11. How do the equations used to represent reactions involved in electrolyses differ from the oxidation-reduction equations studied in Chap. XVIII?

12. Write equations to represent the chemical changes that occur during the electrolysis of aqueous solutions of each of the following substances:

(*a*) Cadmium acetate	(*f*) Potassium phosphate
(*b*) Ferric bromide	(*g*) Stannous chloride
(*c*) Barium hydroxide	(*h*) Chromic nitrate
(*d*) Calcium sulfide	(*i*) Cobalt iodide
(*e*) Aluminum sulfate	(*j*) Sodium sulfite

SUGGESTED READING

Journal of Chemical Education

BENNETT, Simpler Aspects of Electrochemistry, 13, 516 (1936).
BROCKMAN, Fused Electrolytes—an Historical Sketch, 4, 512 (1927).

CHAPTER XXII

INDUSTRIAL ELECTROCHEMICAL PROCESSES

The development of processes for the production of chemicals by electrolysis on an industrial scale has in the past been retarded in some measure by the unavailability of cheap electricity. Consequently, the extensive use of electrochemical processes has been limited largely to regions such as the Niagara Falls area. However, the relatively recent and widespread development of federal power projects such as Boulder Dam and others has already resulted in more extensive use of electrochemical processes, and there is every indication that this phase of the chemical industries will be continuingly expanded in various regions in the United States.

The following sections are concerned with a discussion of a few chemical processes that involve the electrolysis of aqueous solutions or fused salts. It is not intended to provide here any exhaustive treatment of the subject but rather to select a few typical cases which will serve to acquaint the student with the nature, the scope, and the importance of these industries.

22.1. Production of Active Metals

It has already been indicated (Sec. 21.9) that the alkali metals, alkaline earth metals, magnesium and aluminum, may be prepared by electrolysis only in the absence of water, and the same is true of the metal beryllium. Although zinc is more commonly produced by other methods (Sec. 26.7), it may also be produced by electrolysis.

Alkali Metals. All the alkali metals, Li, Na, K, Rb, and Cs, are very light metals which exhibit a silvery metallic luster and have low melting temperatures. These are relatively costly metals as is seen from the fact that the cheapest one, sodium, sells at about 40 cents per pound; while the next in order of cost, potassium, sells at about $12 per pound. All the alkali metals are produced commercially by the electrolysis of their fused chlorides in electrolytic cells, which must be designed especially for each metal. Since sodium is the only alkali metal produced industrially on a large scale, its production will be outlined in some detail.

Practically all of the sodium produced in the United States involves

the use of the Downs cell, a diagram of which is shown in Fig. 95. Fused sodium chloride is electrolyzed between a graphite anode and an annular iron cathode.

$$\begin{array}{rr} \text{Anode:} & 2Cl^- - 2e^- \rightarrow Cl_2^0 \\ \text{Cathode:} & 2Na^+ + 2e^- \rightarrow 2Na^0 \\ \hline \text{Cell:} & 2Na^+Cl^- \rightarrow 2Na^0 + \overset{\uparrow}{Cl_2^0} \end{array}$$

The sodium liberated at the cathode rises to the surface in the annular compartment surrounding the cathode and flows over into the container C, where the sodium is collected under oil and subsequently

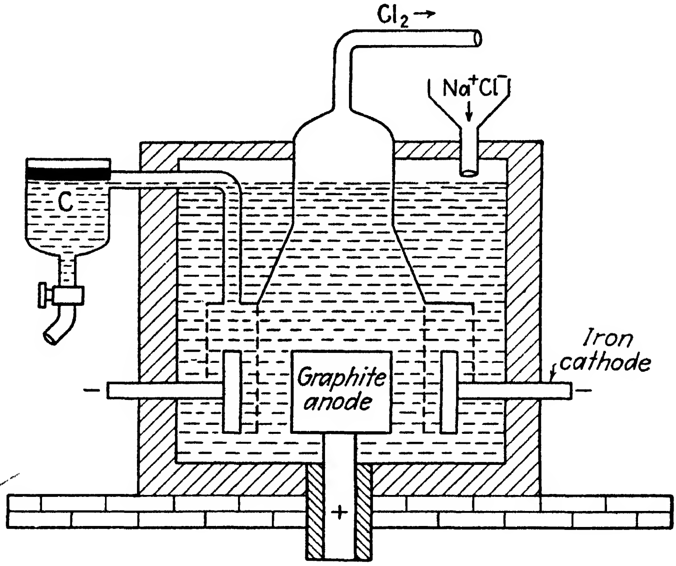


FIG. 95.—Downs cell used in the production of sodium.

withdrawn. The chlorine liberated at the anode is removed from the cell via the exit tube, indicated in Fig. 95, and is collected for sale as elemental chlorine or for use in other chemical processes.

The chief uses of sodium are concerned with the preparation of compounds such as sodium peroxide (Na_2O_2) and sodium cyanide ($NaCN$). Sodium is also used in many preparative procedures for the formation of compounds that do not contain sodium, *e.g.*, tetraethyl lead, dyes, organic medicinals, etc. Electric lamps containing sodium and neon are known as *sodium-vapor lamps*. Such lamps produce a soft penetrating yellow light which is used in the illumination of highways. Although the other alkali metals are used to only a very limited extent, each has certain rather highly specialized uses, *e.g.*, the use of cesium in photoelectric cells and in certain types of radio tubes.

Alkaline-earth Metals. Of these metals, Ca, Sr, and Ba, only calcium is produced commercially in appreciable quantities. These three metals are more difficult to produce than the alkali metals since the chlorides of the alkaline-earth metals melt at relatively high temperatures. Furthermore, when these metals are liberated at the cathode, they tend to become colloidally dispersed throughout the molten electrolyte. Accordingly, it is necessary to design the electrolytic cells in such manner as to permit the immediate collection of the elemental metal. The type of cell used in the production of calcium (Fig. 96) will serve as a suitable illustration. Molten calcium

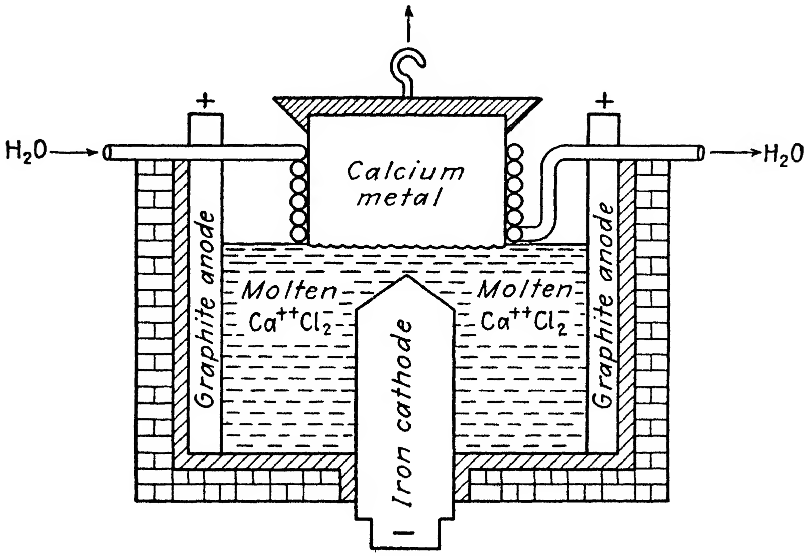


Fig. 96.—Cell for the electrolytic production of calcium.

chloride is placed in a cylindrical vessel around the walls of which are placed several carbon anodes and through the bottom of which extends an iron cathode. Directly above the cathode is placed a bar of calcium in contact with the surface of the electrolyte and cooled by water which flows through pipes that surround the bar. As calcium is liberated at the cathode, it rises through the electrolyte, comes in contact with and adheres to the bar of calcium.

$$\begin{array}{rl} \text{Anode:} & 2Cl^- - 2e^- \rightarrow Cl_2^0 \\ \text{Cathode:} & \underline{Ca^{++} + 2e^- \rightarrow Ca^0} \\ \text{Cell:} & Ca^{++}Cl_2^- \rightarrow Ca^0 + \overline{Cl}_2^0 \end{array}$$

The bar of calcium is slowly withdrawn at a rate equal to that at which the calcium metal is collected. Of course, chlorine is produced at the anode.

The development of extensive uses for the alkaline-earth metals has been retarded by their high cost of production. Nevertheless, these metals are very useful in the chemical laboratory and are used commercially to a limited extent as reducing agents in the production of other metals.

Magnesium. The method most widely used in the production of magnesium involves the electrolysis of fused magnesium chloride in an iron vessel (the walls of which serve as the cathode) into which anodes made of carbon are suspended. The magnesium liberated at the cathode is lighter than the electrolyte and therefore rises to the surface where it is removed mechanically.

Although magnesium metal is used in the manufacture of signal flares, in the removal of gases from radio tubes, and in the production and purification of other metals, the single most important use for this metal lies in the fabrication of alloys (Sec. 25.6). In recent years, many industrial products previously made from heavy metals such as copper and iron have been replaced by alloys of the light metals such as magnesium, beryllium, and aluminum. The increased speed and efficiency of modern transportation facilities (airplanes, automobiles, streamlined trains, etc.) are possible largely through the availability of alloys of the light metals. With the present extensive expansion of transportation by air, it is not unreasonable to suggest that magnesium and aluminum may eventually come to rival the traditional industrial importance of iron.

Zinc. Although it is a fairly active metal, the chemical activity of zinc is markedly less than that of the other metals considered in this chapter. Only about one-fourth of the zinc produced in this country is prepared by electrolysis. The remainder is produced by nonelectrolytic methods which will be described in a subsequent chapter (Sec. 26.7). In the electrolytic process, zinc ores are treated ("leached") with dilute sulfuric acid which extracts the zinc as zinc sulfate. The resulting aqueous solution is electrolyzed between a carbon anode and a cathode consisting of a thin sheet of pure zinc. Oxygen is liberated at the anode. As the electrolysis proceeds, the solution becomes progressively dilute with respect to Zn^{++} and progressively concentrated with respect to $H_2^+SO_4^=$ (Sec. 21.5). Consequently, the aqueous electrolyte may finally be used to treat a new batch of zinc ore.

Zinc is used chiefly as a protective coating for other metals (Sec. 26.7) and in the manufacture of alloys such as bronzes, brass, and bearing metals. Lesser quantities of zinc are used in the manufacture of dry-cell batteries (Sec. 23.8), and as a reducing agent both for small-

scale laboratory use and in the industrial production of less active metals such as silver.

Aluminum. It is a significant fact that chemical industries are characterized by ever-increasing quality of products accompanied by ever-decreasing prices. This trend is perhaps no better illustrated than by the history of the production of aluminum. This metal was first prepared in Denmark in 1825 by the reduction of aluminum chloride by potassium at elevated temperatures.

$$AlCl_3 + 3K \rightarrow Al + 3KCl$$

The aluminum so produced sold for $158 per pound owing to the high cost of potassium and to the expense involved in obtaining dry aluminum chloride. Substitution of the cheaper metal sodium for the potassium lowered the price of aluminum to around $25 per pound while subsequent improvements in methods for the production of sodium made possible the sale of aluminum at $5 per pound. Even so, these improved methods resulted in a total production of less than 100 lb. of aluminum during the years in which these methods were used.

Fig. 97.—Charles Martin Hall (1863–1914).

While still an undergraduate student at Oberlin College, Charles Martin Hall (Fig. 97) became interested in the problem of producing aluminum efficiently and at low cost. Using makeshift equipment and working under many handicaps, he successfully devised the electrolytic process that has come to bear his name. Hall first produced aluminum in 1886 and its price soon thereafter dropped to about 20 cents per pound. In the Hall process, the cell proper consists of an iron box lined with carbon which serves as the cathode; a series of carbon rods extending into the vessel serve as the anode (Fig. 98). The vessel is charged with the mineral *cryolite* (Na_3AlF_6) (sodium aluminum fluoride) which is melted by the heat generated by the electric current from the generator. To the melted cryolite is then added aluminum oxide (Al_2O_3) obtained from the ore known as *bauxite*

($Al_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot 2H_2O$). The oxide dissolves in the sodium aluminum fluoride and serves as the electrolyte. Thus, the molten cryolite serves as the solvent and aluminum oxide as the solute. During electrolysis aluminum liberated at the cathode settles to the bottom of the cell and is withdrawn at suitable intervals. Of the oxygen liberated at the anode, some escapes as such while a part reacts with the carbon anodes to form oxides of carbon. As the dissolved aluminum oxide is electrolyzed, provision is made for addition of more Al_2O_3 at regular intervals so that the cells may be operated continuously.

Using the Hall process exclusively, the aluminum industry in the United States alone produces more than 150,000 tons of aluminum each year, and it is impossible to estimate the magnitude of probable

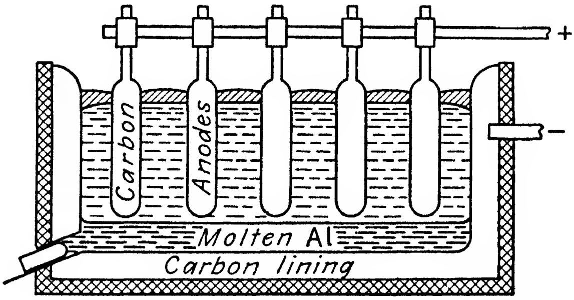


FIG. 98.—Production of aluminum by the Hall process.

future production. The commercial product obtained directly by electrolysis has a purity greater than 99 per cent. It is of interest to note that a few months following the discovery of the Hall process, an identical method was discovered independently by the French chemist, Heroult.

The uses of aluminum are those characteristic of the light metals, some of which uses have already been pointed out in connection with the discussion of magnesium (see above). Aluminum is also used in fabricating wire cables for electric-power transmission lines, in the manufacture of kitchen utensils, furniture, paint, and a wide variety of other useful articles. In connection with the general topic of alloys (Sec. 25.6) attention will be called to several important alloys containing aluminum.

22.2. Electrolytic Refining of Copper

A large percentage of the metallic copper produced is used in the form of copper wire for the conduction of electricity. For this purpose, copper must be rendered very pure since the electrical conductivity of copper increases with increase in purity. Copper produced by the

usual chemical methods (Sec. 26.1) is not sufficiently pure for this purpose and is therefore subjected to an electrolytic refining process. Crude copper in the form of large slabs (Fig. 99) serves as the anode, and a thin sheet of pure copper serves as the cathode in an electrolytic cell in which an aqueous solution of copper sulfate containing an excess of dilute sulfuric acid is used as the electrolyte. The chief impurities in the crude copper anode consist of Zn, Ni, Fe, Ag, Au, Pt, and Pd. During electrolysis the anode dissolves to form Cu^{++}, Zn^{++}, Ni^{++}, and Fe^{++}, and the applied voltage from the generator is so regulated that only the copper is deposited on the cathode, leaving the Zn^{++}, Ni^{++}, and Fe^{++} (which are present in relatively small amounts) in solution. At the same time, the less active metals, Ag, Au, Pt, and Pd do not dissolve to form ions and hence simply settle to the bottom of the cell

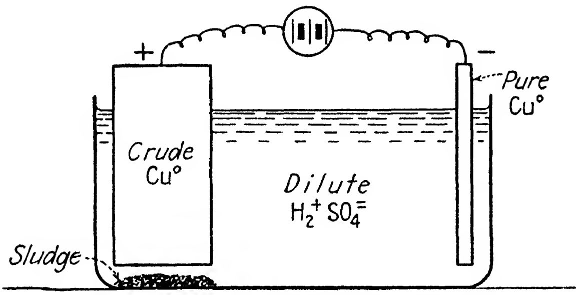


FIG. 99.—Electrolytic refining of copper.

where they collect in the form of a "sludge." The copper which is deposited on the cathode is usually at least 99.9 per cent pure.

Each industrial chemical process has as its objective the economical production of a particular primary product. It is frequently true that, in attaining this objective, one or more by-products may become available. If these by-products can be disposed of at a profit, this serves to decrease the over-all cost of operation and to permit the sale of the primary product at a lower, more favorable competitive price. Thus, the cost of electrolytically refined copper is dependent upon the recovery and sale of the by-products, silver, gold, platinum, and palladium. These so-called *precious metals* are recovered in large quantities from accumulated "anode sludges." Fully one-fourth of the total production of silver, about one-eighth of the gold, and lesser quantities of platinum and palladium are obtained as by-products of the electrolytic refining of copper.

22.3. Electroplating Industries

Everyone is aware of the fact that, if objects made of iron, steel, or other metals or alloys are allowed to remain in contact with air and

atmospheric moisture, their surfaces become tarnished, "rusted," or corroded. The practice of placing (by electrolysis) a protective metallic coating upon such objects constitutes one of the oldest of the electrochemical industries. The metal comprising the protective coating usually consists of less active metals such as silver, gold, platinum, chromium, nickel, or copper. Electroplating is sometimes done merely for the purpose of improving the appearance of the finished product. In the process of electroplating silver on the surface of table cutlery, for example, the object to be plated is made the cathode of the electrolytic cell (Fig. 100). A sheet of pure silver constitutes the anode, which dissolves at the same rate that silver is deposited on the cathode. The electrolyte consists of potassium argentocyanide [$KAg(CN)_2$].

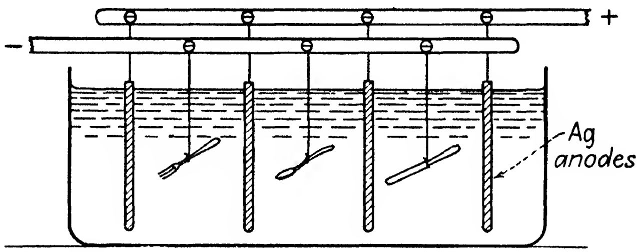


FIG. 100.—The electroplating of table cutlery with silver.

In this as in most other electroplating operations, it is desired to obtain a firm adherent deposit of metal which can thereafter be burnished or polished. In order to secure such a deposit, careful regulation of temperature, current, concentration of electrolyte, and *rate* of deposition must be maintained throughout the entire electrolysis. Failure to control any one or more of these variables usually results in flaky or crumbly nonadherent deposits.

In a similar manner, copperplating is accomplished using a copper anode and a solution of potassium cuprocyanide [$KCu(CN)_2$] as the electrolyte. Nickel is usually plated from nickel ammonium sulfate solutions [$Ni(NH_4)_2(SO_4)_2$] while the electrolyte used in chromium plating consists of a mixture of chromic acid (H_2CrO_4) and chromic sulfate [$Cr_2(SO_4)_3$]. The case of chromium serves as a good example of the problems frequently encountered in the electroplating industries. In order to place a bright, attractive, and yet highly protective coating on objects such as automobile bumpers and headlights, it is desirable to coat the original iron or steel object with chromium. However, since chromium does not adhere readily to iron, the iron is first coated with nickel and finally with chromium.

22.4. Electrolytic Production of Nonmetallic Elements

With the single exception of fluorine, the nonmetallic elements are usually more conveniently prepared by nonelectrolytic methods, some of which will be described in detail in a later chapter. However, certain nonmetals are produced in sufficient quantity by electrolytic methods to warrant their consideration here.

Hydrogen and Oxygen. From the preceding sections together with Chap. XXI, it should be apparent that oxygen and hydrogen may often appear as by-products of industrial electrochemical processes in which nondischargeable anions and cations are involved. Whether these elements are collected and used depends, in any case, upon the costs involved and the competition offered by other methods of production. Since oxygen can be produced so readily and at such low cost from liquid air (Sec. 4.1), but little oxygen is produced commercially by other methods. A considerable quantity of hydrogen is produced as the primary product together with by-product oxygen by the electrolysis of aqueous sodium hydroxide solution. The electrolytic cell employs an iron cathode and a nickel anode. The products, hydrogen and oxygen, are the same as those resulting from the electrolysis of water, dilute sulfuric acid, etc. (Sec. 21.5). Large quantities of hydrogen are also produced as a by-product of the electrolysis of aqueous sodium chloride solution.

Halogens. As will be pointed out in Sec. 22.5, an important industrial method for the production of chlorine is perhaps more significant in terms of the primary product, sodium hydroxide. Of course, chlorine, bromine, and iodine may be formed by the electrolysis either of aqueous or fused chlorides, bromides, or iodides. However, with the exception of chlorine, these elements are more commonly produced by other methods.

Fluorine can be produced only by electrolysis, and then only with difficulty. The complications involved in its production arise from the extreme chemical activity of this element. Of all the known elements, fluorine has the greatest affinity for electrons; hence, it is the most powerful oxidizing agent (electron acceptor). Accordingly, fluorine cannot be prepared by the oxidation of fluorine compounds since this would require an oxidizing agent more powerful than fluorine. This element displaces oxygen from water, attacks all but the very unreactive metals such as platinum, and forms compounds with all elements except the inert gases. Because of its generally corrosive character, the design of apparatus for the preparation, storage, and use of fluorine presents many difficult problems. The element is pre-

pared by the electrolysis of fused potassium hydrogen fluoride (KHF_2) in a copper cell which serves as a cathode and which is fitted with graphite anodes (Fig. 101). Although cells made of copper are fairly resistant to attack by fluorine, they last for only a short time. More durable cells may be made of silver, platinum, or gold.

The importance of fluorine lies largely in the use of several compounds of that element. Calcium fluoride (CaF_2) (*fluorspar*) is used as a flux and like sodium fluoride (NaF) as an insecticide. Ammonium fluoride (NH_4F) is used as a disinfectant, hydrofluoric acid is used in the etching of glass, and organic fluorine compounds are used as commercial refrigerants.

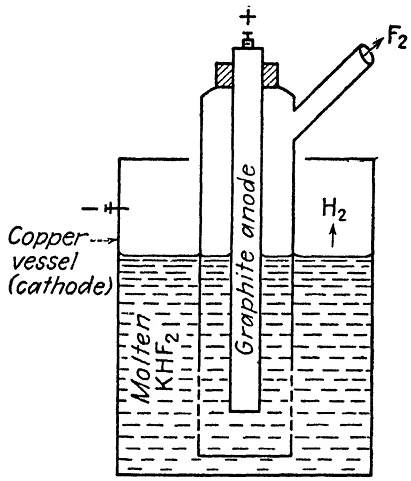


FIG. 101.—Cell for the production of fluorine by the electrolysis of potassium hydrogen fluoride.

22.5. Electrolytic Production of Compounds

Only a small number of compounds are produced directly by electrolysis. To illustrate this type of process, the electrolytic production of sodium hydroxide will be described in detail, and it will thereafter be shown how this process may be modified to permit the formation of two other valuable commercial chemicals.

Sodium Hydroxide. The electrolysis of an aqueous solution of sodium chloride yields chlorine at the anode and hydrogen at the cathode. Discharge of hydrogen ions (from water) leaves sodium and hydroxyl ions in the region surrounding the cathode. Thus, sodium hydroxide is produced in the solution about the cathode. The use of this method for the production of both chlorine and sodium hydroxide depends upon the devising of some means of keeping the chlorine and sodium hydroxide from coming into contact since they react to form other compounds (see below). Of the numerous cells designed to accomplish this purpose, one used rather widely is the Nelson cell (Fig. 102).

The walls of the vessel that serves as the container for the salt solution (brine), and as the cathode, consist of perforated sheets of iron or of wire gauze covered on the *inside* with layers of asbestos paper. The anodes, composed of graphite, are immersed in the solution in the

center of the cell. The thickness of the asbestos paper and the height of the liquid in the cell are such that the aqueous solution seeps through the paper and reaches the cathode just fast enough to sweep the hydroxyl ions to the back of the cathode as rapidly as they are left behind by the discharge of hydrogen ions. The liquid at the back of the cathode takes no further part in the electrolysis and drops off the cathode and into the vessel placed below the cathode. At the same time, the chlorine gas liberated at the anode rises into the space above the solution, from which the gas is withdrawn by slight suction. Thus, the chlorine is collected inside the asbestos walls where it cannot

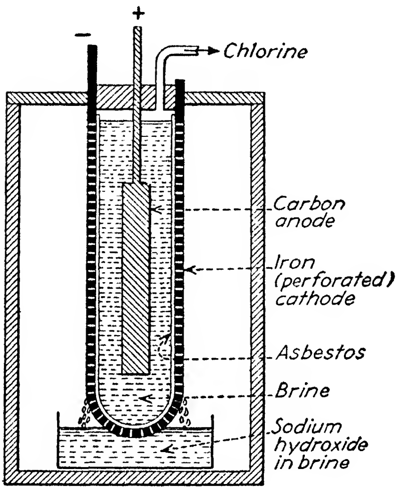


Fig. 102.—The Nelson cell.

come into contact with the sodium hydroxide. In the operation of the Nelson cell, provision is made for continuous operation by adding fresh brine automatically.

In this cell, not all of the dissolved sodium chloride is electrolyzed. Consequently, the solution that seeps through the perforated cathode contains sodium hydroxide together with some unchanged sodium chloride. The solution is concentrated by evaporation, whereupon most of the less soluble sodium chloride crystallizes, while the very soluble sodium hydroxide remains in solution. This concentrated solution of sodium hydroxide (caustic soda) may be sold as such or the remainder of the water may be driven off by heating to form solid sodium hydroxide. If a purer product is desired, the solid is dissolved in alcohol, which will not dissolve the remaining traces of sodium chloride. Pure sodium hydroxide is then secured by filtration followed by evaporation of the alcohol.

Another somewhat more complicated cell for the production of chlorine and sodium hydroxide by the electrolysis of sodium chloride solution is the Castner-Kellner cell, which employs a liquid mercury cathode.

Sodium Hypochlorite. If, in the electrolysis of sodium chloride solution, provision is made for the intimate mixing of the chlorine and sodium hydroxide at low temperatures, the following reaction occurs:

$$\overline{Cl}_2^0 + 2Na^+OH^- \rightarrow Na^+ClO^- + Na^+Cl^- + H_2O$$

The resulting aqueous solution containing sodium chloride and sodium hypochlorite is known as *Javelle water* and is used as an antiseptic (Dakin's solution). Treatment of Javelle water with a strong acid results in liberation (in solution) of the weak and unstable hypochlorous acid,

$$2Na^+ClO^- + H_2^+SO_4^= \rightarrow 2HClO + Na_2^+SO_4^=$$

which decomposes readily to liberate oxygen and which is used extensively as a bleaching agent.

Sodium Carbonate. When sodium hydroxide is produced by the electrolysis of sodium chloride solution saturated with carbon dioxide, sodium carbonate is produced as follows:

$$\overline{CO}_2 + H_2O \rightleftharpoons H_2CO_3$$
$$Na^+OH^- + H_2CO_3 \rightarrow H_2O + Na^+HCO_3^-$$

If the quantity of available carbon dioxide is limited, the normal carbonate results.

$$2Na^+OH^- + H_2CO_3 \rightarrow 2H_2O + Na_2^+CO_3^=$$

Although this electrolytic method has many advantageous features in comparison with other methods (Sec. 32.3 and 32.4), it suffers the competitive disadvantage of high electrical-power costs.

EXERCISES

1. Assuming that a given chemical reaction is being considered as the basis for establishment of manufacturing operations, what characteristics of the reaction will determine the economic feasibility of its use on a commercial scale?

2. Suggest several factors that might influence the choice of location for *any* industrial chemical process.

3. Why are the more active metals most commonly prepared by the electrolysis of fused salts?

4. What fact would make it seem unwise economically to build a plant dessigned to produce chlorine as the only product?

5. Show how the selling price of copper is influenced by the market price of silver and gold.

6. In what essential respect does the production of aluminum differ from other processes in which metals are produced by the electrolysis of fused salts?

7. Why is it possible to purify copper by electrolysis of solutions that contain dischargeable cations other than copper?

8. Advance arguments in support of the view that metals such as zinc, iron, and copper are more precious than gold, silver, etc.

9. What experimental conditions determine the success of electroplating operations?

10. On the basis of a comparison of the structures of the atoms of F, Cl, Br, and I, suggest a reason why fluorine might be expected to be (*a*) the most active of the halogens and (*b*) the strongest oxidizing agent known.

11. Suggest a plan whereby four important chemicals might be produced from water and only one other raw material.

12. Upon what one feature of the Nelson cell does the successful use of this apparatus depend?

13. List important uses for each of the following: (*a*) Javelle water, (*b*) sodium (*c*) aluminum, (*d*) magnesium, (*e*) zinc, (*f*) copper, (*g*) fluorine.

14. Write (in steps) the equation for the oxidation-reduction reaction involved in the electrolytic production of sodium hypochlorite. List the name of the oxidizing agent and the reducing agent.

SUGGESTED READING

Journal of Chemical Education

ANON, Versatile Scavenger (Calcium), **19,** 504 (1942).
ST. PETER, The Light Metals: Aluminum and Magnesium, **19,** 556 (1942).
HOLMES, The Story of Aluminum, **7,** 233 (1930).
HOBBS, Some Commercial Applications of Aluminum, **7,** 245 (1930).
FINK, Electrochemistry of the Rare Metals, **16,** 108 (1939).
RICH, The Future of Electroforming, **19,** 386 (1942).

Industrial and Engineering Chemistry

GANN, The Magnesium Industry, **22,** 694 (1930).
CHESNY, Magnesium Compounds from Ocean Water, **28,** 383 (1936).
KILLEFFER, Chromium Plating—A New Aid to Industry, **19,** 773 (1927).
BARNARD, Silver Plating of Optical Glassware, **34,** 637 (1942).

Metals and Alloys

RAY, The Electrolytic Preparation of Alloys of Barium and Strontium, **1,** 112 (1929).

Chemical and Metallurgical Engineering

RAMSEY, Magnesium Production at the World's Largest Plant, **50,** 98, 115 (1943).

CHAPTER XXIII

BATTERY CELLS

Every one is familiar with the use of storage batteries in automobiles, the use of the so-called *dry cell* in flashlights, etc. In connection with the study of electrolysis (Sec. 21.1), attention was called to the possibility of employing storage batteries as the source of electrical energy necessary for the occurrence of electrochemical transformations. In view of the fact that the energy supplied by a battery cell is of chemical origin, it becomes of interest to inquire into the manner in which the energy originating in chemical reactions can be utilized in the performance of useful work. Such an inquiry will serve also to establish the relationship between the chemical changes that occur during electrolysis and those which take place in battery cells.

23.1. Relationship between Electrolytic Cells and Battery Cells

Perhaps the best approach to an understanding of the operation of battery cells may be had by reconsidering a simple case of electrolysis. As has already been shown (Sec. 21.2), the nonspontaneous changes that occur during the electrolysis of an aqueous solution of zinc chloride may be represented by the following equations:

$$\begin{array}{rl} \text{Anode:} & 2Cl^- - 2e^- \rightarrow Cl_2^0 \\ \text{Cathode:} & \underline{Zn^{++} + 2e^- \rightarrow Zn^0} \\ \text{Cell:} & Zn^{++}Cl_2^- \rightarrow \underline{Zn^0} + \overline{Cl_2^0} \end{array}$$

These changes are caused to occur by the imposition of an outside force which may take the form of electrical energy supplied by a battery cell. Thus, energy is utilized and work is done in electrolyzing the zinc chloride solution. Since energy may be neither created nor destroyed, it follows that the electrical energy utilized during electrolysis must have been transformed into chemical energy possessed by the products of electrolysis. This fact leads directly to the question as to whether this chemical energy stored up in the products of electrolysis (zinc and chlorine) may be retransformed into electrical energy. In other words, it is proposed to electrolyze zinc chloride solution in a suitable cell and thereafter to use this cell as a source of energy, *i.e.*, as a battery. The feasibility of this suggestion may be

ascertained by electrolyzing a zinc chloride solution until an appreciable quantity of the products of electrolysis has been accumulated and thereafter connecting the electrodes to a voltmeter as indicated in Fig. 103. (Of course, some of the chlorine gas will have been lost, but enough chlorine will be dissolved in the water surrounding the anode of the electrolytic cell, and contained within the glass housing placed about the carbon anode, to enable one to secure the desired information.) It is found that the cell in question is capable of functioning as a battery which delivers a voltage of about 2.1 volts.

As one continues to draw current from this battery, it may be shown that zinc dissolves off the electrode and goes into solution as Zn^{++}. Hence, at that electrode which shall be designated as the

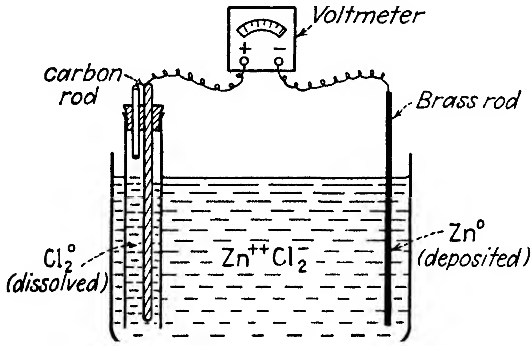


Fig. 103.—Battery resulting from the electrolysis of zinc chloride solution.

negative (−) terminal of the battery, electrons are made available by the occurrence of the oxidation reaction,

$$(-)\text{ Terminal: } Zn^0 - 2e^- \rightarrow Zn^{++}$$

which represents the normal tendency toward spontaneous loss of electrons by zinc in its effort to approach the electronic structure of the nearest inert gas, argon. Correspondingly, the reaction at the positive (+) terminal of the battery involves the reduction reaction,

$$(+)\text{ Terminal: } Cl_2^0 + 2e^- \rightarrow 2Cl^-$$

which corresponds to the spontaneous reaction tendency normally exhibited by chlorine, as atoms of this element seek additional electrons that enable each chlorine atom to acquire an extra-nuclear structure like that of an inert gas. Thus, electrons flow from the negative terminal through the outside circuit (including the voltmeter) and over to the positive terminal. This is just the opposite of the direction of flow of electrons during electrolysis, and the oxidation-reduction

reactions representing the changes that occur in the battery cell,

$$\begin{array}{rl} (-)\ \text{Terminal:} & Zn^0 - 2e^- \rightarrow Zn^{++} \\ (+)\ \text{Terminal:} & \underline{Cl_2^0 + 2e^- \rightarrow 2Cl^-} \\ \text{Battery:} & Zn^0 + Cl_2^0 \rightarrow Zn^{++} + 2Cl^- \end{array}$$

are also seen to be the reverse of those which occur during the electrolysis of zinc chloride solution.

Although a battery cell depending upon these reactions of zinc and chlorine could be used as a source of electrical energy, it is rather obvious that a battery involving the use of gaseous chlorine would hardly be practical in everyday use. Hence, before going any further into the problem of the general characteristics of battery cells, a battery more nearly suitable for actual use will be considered.

23.2. Daniell Cell

One may construct a Daniell cell quite simply by immersing a strip of zinc metal in an aqueous solution of zinc sulfate contained in a porous unglazed porcelain cup and similarly immersing a strip of copper in an aqueous solution of copper sulfate in a similar container. When these two units are then placed in a container partly filled with a solution of an electrolyte such as sodium chloride, and the two terminals are connected to a voltmeter, as shown in Fig. 104, it is observed that a voltage of 1.102 volts is produced.

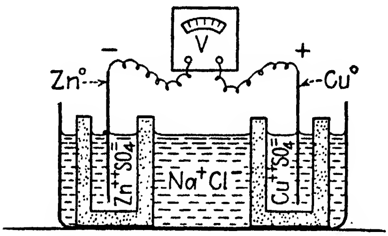


FIG. 104.—The Daniell cell.

It is immediately apparent that the Daniell cell differs from the zinc-chlorine battery in that the electrode materials of the former (*i.e.*, zinc and copper) are both metals that normally exhibit a tendency to lose electrons. If the Daniell cell is to function as a battery, both metals cannot lose electrons—one must lose and the other must gain electrons. In this particular case, the issue may be decided qualitatively at least, in terms of the order of activity of the metals (Sec. 8.2). From Table 8, it will be recalled that zinc is much more active chemically than copper; hence zinc might be expected to lose electrons more readily than copper if the metals are in contact with solutions of their ions at the same concentration. It may be inferred correctly that the reactions that occur when the Daniell cell serves as a source of electrical energy are

$$\begin{aligned} (-)\ \text{Terminal:}\quad & Zn^0 - 2e^- \rightarrow Zn^{++} \\ (+)\ \text{Terminal:}\quad & Cu^{++} + 2e^- \rightarrow Cu^0 \\ \hline \text{Battery:}\quad & \underline{Zn^0} + Cu^{++} \rightarrow Zn^{++} + \underline{Cu^0} \end{aligned}$$

From this it may be seen that the reactions that occur at the two terminals of a battery employing metals as both terminals are dependent upon the relative tendencies of the two metals toward loss of electrons. Consequently, any further study of battery cells should be based upon some suitable *quantitative* expression of these tendencies.

23.3. Electrode Potentials

The atoms of all the elements have *some* tendency toward loss of electrons. In the case of the nonmetallic elements, this tendency is extremely small in relation to their tendency to gain electrons. Consider, for example, the tendencies exhibited when a strip of metallic zinc is placed in contact with a solution containing zinc ions (Fig. 105). Atoms of zinc tend to detach themselves from the surface of the metal and go into solution as zinc ions by losing electrons. At the same time, zinc ions in the solution tend to acquire electrons at the surface of the metal and become zinc atoms. Thus in the case of zinc, there are two opposing tendencies, the larger of which is that toward loss of electrons. An equilibrium between these two tendencies becomes established and, since the tendency toward loss of electrons predominates, the strip of zinc possesses an excess of electrons and may be said to have acquired a negative electrical potential, *i.e.*, there will be a difference of potential between the metal and the solution. For zinc or for any other substance in contact with a solution of its ions, the magnitude of this difference in potential depends upon both temperature and concentration. This must be true since the return of ions from the solution to the metal depends upon the velocity with which the ions move through the solution and upon the number of collisions that occur between the ions and the surface of the metal. The higher the temperature, the greater will be the speed of the ions, and the greater the concentration, the greater will be the number of collisions per unit of time.

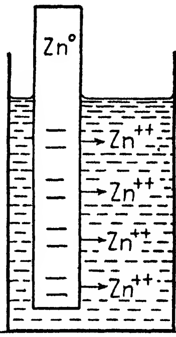


Fig. 105.—A zinc electrode in equilibrium with a solution containing zinc ions acquires a negative potential.

If, on the other hand, a strip of copper is placed in contact with a solution of copper ions (Fig. 106), the same tendencies are exhibited. Although copper atoms do tend to lose electrons and become copper ions, this is opposed by a greater tendency for copper ions to gain electrons and become copper atoms. Hence in this case, the copper electrode acquires a positive potential with respect to the solution. Accordingly, the electrode potential of copper is given a positive sign while that of zinc is given a negative sign, from which it follows that the sign of an electrode potential indicates which of these two tendencies predominates.

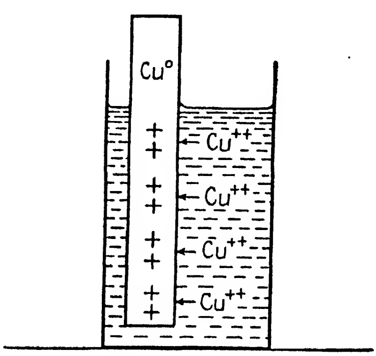


Fig. 106.—A copper electrode in equilibrium with a solution containing copper ions acquires a positive potential.

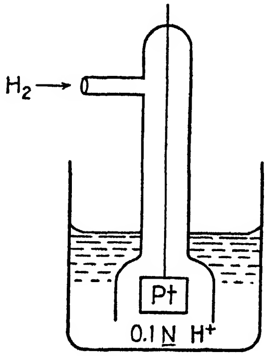


Fig. 107.—A common type of hydrogen electrode.

Measurement of Electrode Potentials. It is not practical to attempt to measure the absolute potential difference between each element and a solution of its ions. Rather, a suitable reference electrode is chosen, and other electrode potentials are measured in relation to this standard. Ordinarily, the hydrogen electrode (Fig. 107) is used as the reference, this electrode consisting of a platinum foil immersed, at 25°C., in a solution which is 0.1 N with respect to hydrogen ions and which is so constructed as to permit hydrogen gas (under a pressure of 1 atm.) to be bubbled into the solution. The potential of this electrode is arbitrarily assumed to have the value of zero. To measure the potential of the zinc electrode, for example, the hydrogen electrode constitutes one-half of the complete cell, as shown in Fig. 108. The other half of the cell consists of the zinc strip in contact with a 1 molal solution of zinc ions. Thus, one actually measures not the absolute potential of the zinc electrode but rather the net effect due to the potential difference between zinc and its ions and that between elemental hydrogen and hydrogen ions. However, since one is interested

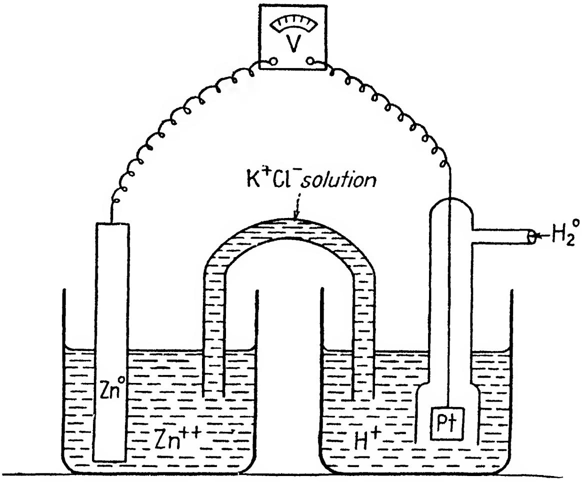


FIG. 108.—Measurement of the potential of a zinc electrode.

TABLE 26
ELECTRODE POTENTIALS*

Element	Equilibrium at electrode	Potential, volts
Potassium	$K^0 \rightleftharpoons K^+ + 1e^-$	−2.922
Barium	$Ba^0 \rightleftharpoons Ba^{++} + 2e^-$	−2.90
Calcium	$Ca^0 \rightleftharpoons Ca^{++} + 2e^-$	−2.763
Sodium	$Na^0 \rightleftharpoons Na^+ + 1e^-$	−2.712
Magnesium	$Mg^0 \rightleftharpoons Mg^{++} + 2e^-$	−2.40
Aluminum	$Al^0 \rightleftharpoons Al^{+++} + 3e^-$	−1.70
Manganese	$Mn^0 \rightleftharpoons Mn^{++} + 2e^-$	−1.10
Zinc	$Zn^0 \rightleftharpoons Zn^{++} + 2e^-$	−0.758
Chromium	$Cr^0 \rightleftharpoons Cr^{++} + 2e^-$	−0.557
Iron	$Fe^0 \rightleftharpoons Fe^{++} + 2e^-$	−0.44
Cadmium	$Cd^0 \rightleftharpoons Cd^{++} + 2e^-$	−0.397
Nickel	$Ni^0 \rightleftharpoons Ni^{++} + 2e^-$	−0.22
Tin	$Sn^0 \rightleftharpoons Sn^{++} + 2e^-$	−0.13
Lead	$Pb^0 \rightleftharpoons Pb^{++} + 2e^-$	−0.12
Hydrogen	$\frac{1}{2}H_2^0 \rightleftharpoons H^+ + 1e^-$	0.00
Bismuth	$Bi^0 \rightleftharpoons Bi^{+++} + 3e^-$	+0.20
Copper	$Cu^0 \rightleftharpoons Cu^{++} + 2e^-$	+0.344
Silver	$Ag^0 \rightleftharpoons Ag^+ + 1e^-$	+0.799
Mercury	$Hg^0 \rightleftharpoons Hg^{++} + 2e^-$	+0.86
Platinum	$Pt^0 \rightleftharpoons Pt^{++++} + 4e^-$	+0.863
Gold	$Au^0 \rightleftharpoons Au^{+++} + 3e^-$	+1.36

* The electrode potentials listed in this table correspond to measurements involving half cells in which each metal was in contact with a 1 molal solution of its ions at 25°C.

primarily in comparing the potential of one electrode with that of another, the constant error involved in assuming the potential of the hydrogen electrode to be zero does not detract from the utility of the electrode potential values obtained in this manner. By making a series of such measurements using a variety of electrodes in comparison with the hydrogen electrode, an extensive list of electrode potential data may be compiled. Such a list is given in Table 26

A comparison of Table 26 with the order of activity of metals (Sec. 8.2) will reveal that the two are identical so far as the positions of the various metals (and hydrogen) are concerned.

In terms of the data of Table 26, the voltage produced by the Daniell cell is seen to be the *sum* of the negative potential of the zinc electrode and the positive potential of the copper electrode, *i.e.*, $0.758 + 0.344 = 1.102$ volts. The voltage produced by a battery involving a cadmium and a lead electrode would be the *difference* between the two potentials (*i.e.*, $0.397 - 0.12 = 0.277$ volt) since both of these electrodes are negative with respect to solutions of their ions.

23.4. Construction of Battery Cells

Any consideration of the requirements to be fulfilled in the construction of battery cells should recognize first that the substances used as electrodes may be but need not be produced by electrolysis. In the earlier discussion of the zinc-chlorine battery (Sec. 23.1) both of the substances involved at the two terminals were considered to be the products of a previously conducted electrolysis. However, the zinc-chlorine battery could just as well have been constructed by the use of zinc and chlorine produced by entirely nonelectrolytic methods. The student will recall that, in connection with the description of the Daniell cell (Sec. 23.2), no specifications were made with regard to the origin of any of the chemicals involved. This freedom to select suitable materials regardless of their origin or past history follows from the fact that the changes that occur during the production of current by a battery are entirely spontaneous, *i.e.*, zinc has a certain tendency to lose electrons which is the same irrespective of the origin of the zinc.

Since suitable arrangement of two substances having different tendencies toward loss of electrons should result in a battery cell, the number of possible batteries would seem to be almost without limit. In constructing such batteries, certain broad requirements must be recognized. These will be enumerated before considering the relative practicality of the many batteries that might conceivably be constructed.

1. *A battery requires two "half cells," each of which must involve two valence states of an element.* Thus, in the Daniell cell, one half cell consists of copper metal (valence = 0) in contact with copper ions (valence = 2+), while the other consists of zinc metal (valence = 0) and zinc ions (valence = 2+). Although often convenient, one component having zero valence is not required. For example, a battery could be constructed so as to involve ferrous (Fe^{++}) and ferric (Fe^{+++}) ions, thus meeting the requirement stated above.

2. *The two solutions surrounding the terminals must either be in contact or must be connected by a solution of an electrolyte.* Examples of suitable arrangements are furnished by the preceding discussions and by those to follow. The function of the electrolyte between the two terminals is exactly the same as that discussed in connection with the study of electrolysis, *viz.*, the maintenance of electrical neutrality in the region of the electrodes. This is accomplished by the transport of ions through the solution.

3. *The negative terminal of the battery is that involving the substance having the greater tendency to lose electrons.* Electrons must therefore be acquired at the other terminal which is designated as the positive terminals.

4. *The voltage delivered by a battery is determined by the innate tendencies of the active materials to lose electrons and by the concentration of these materials.* In Table 26, the listed numerical values representing the various electrode potentials were obtained experimentally under comparable conditions of concentration and temperature. The relative position of any electrode included in that list would be changed if the experimental measurements were made using a sufficiently different concentration of ions surrounding the electrode. The influence of a change in concentration upon these equilibria is wholly in accord with facts presented earlier in connection with the study of reversible reactions and equilibria (Sec. 12.6).

Practical Batteries. In the manufacture of batteries for the performance of useful work, convenience, cost, and durability are the major considerations. Since so-called *storage* batteries generally involve the use of aqueous solutions of electrolytes, very active metals such as sodium, potassium, and calcium are excluded since these metals displace hydrogen from water. The very active nonmetal, fluorine, is also excluded since it displaces oxygen from water. The gaseous elements and compounds are also impractical since provision for the use of gases in batteries for everyday application would be very difficult. With these exclusions, it follows that practical batteries usually employ electrodes consisting of the solid elements (both metals

and nonmetals) and their solid compounds in contact with electrolytes in aqueous solutions the cencentration of which may be varied over wide ranges.

If one wishes to construct a battery to deliver a given voltage, the initial selection of the electrode materials may be made by reference to a tabulation of electrode potentials, such as is given in Table 26. For example, if a 2.0-volt cell is desired, the use of manganese and mercury terminals would be indicated since this combination (see Table 26) would produce $1.10 + 0.86 = 1.96$ volts. By suitable adjustment of the concentration of the electrolytes surrounding the two terminals, exactly the required voltage could be obtained. If one wished to consider electrodes other than the metals listed in Table 26, reference should be made to more extensive tables of data.

From a consideration of the nature of the changes that occur while a battery is in use as a source of energy, it may be seen that the negative terminal is dissolved while the concentration of the ions corresponding to the positive terminal is progressively decreased as these ions are converted to the corresponding neutral atoms that are deposited at the surface of the positive terminal. Hence the useful life of a battery would appear to be limited by the available supply of the materials that react (spontaneously) at the two terminals. This is not the case if the battery is one capable of being "charged." While a battery is delivering current, it is said to be undergoing a process of *discharge*. Reversal of the reactions that occur during discharge constitutes the process of *charging* the battery, which is accomplished by electrolysis. In effect, the production of the zinc-chlorine battery consisted in the charging of that battery. If the battery was then used as a source of current until all or nearly all of the zinc and chlorine was used up, the cell could be charged again by repeating the process of electrolysis. To charge a battery capable of providing any given voltage, it is necessary only to connect the terminals to the corresponding terminals of another battery (or more likely a generator) capable of producing a higher voltage. Examples of batteries that may not be recharged conveniently are the Daniell cell and the common dry cell. The familiar lead storage battery owes much of its utility to the ease with which it may be recharged.

23.5. Gravity Cell

The gravity or crowfoot battery (Fig. 109) is merely a special case of the Daniell cell (Sec. 23.2) and involves identically the same reactions. The gravity cell is constructed by surrounding thin sheets of copper (which serve as the positive terminal) by a saturated solu-

tion of copper sulfate together with an excess of solid crystals of $CuSO_4 \cdot 5H_2O$. The solution surrounding the negative terminal consists of a *dilute* solution of zinc sulfate having a specific gravity so much less than that of the *concentrated* copper sulfate solution that the two solutions do not mix appreciably; hence the name *gravity* cell. A heavy zinc electrode (the negative terminal) is fashioned in the form of a crowfoot in order to present an extensive surface area and is immersed in the dilute zinc sulfate solution. When the two terminals are connected, electrons flow from the zinc to the copper electrode. The initial voltage supplied amounts to 1.102 volts. However, as the

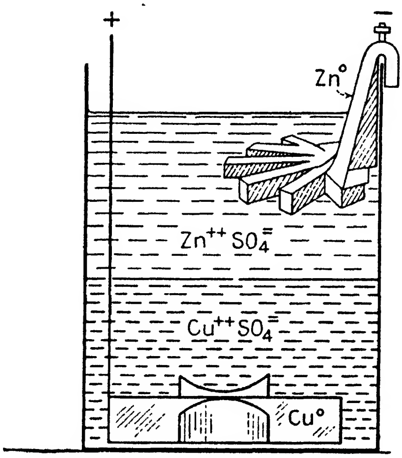


Fig. 109.—The gravity cell.

battery continues to deliver current, the zinc electrode dissolves and the surrounding solution becomes progressively more concentrated, hence, the zinc electrode becomes less negative with respect to the solution and the voltage drops off in proportion. It is neither convenient nor practical to attempt to recharge a gravity cell.

23.6. Lead Storage Battery

This battery is the one so commonly used in automobiles as well as in numerous other applications that require relatively small voltages. The essential parts of the lead storage battery are shown in Fig. 110. As constructed commercially, a hard rubber case contains dilute sulfuric acid of initial specific gravity equal to from 1.250 to 1.275 which serves as the electrolyte. The negative terminal consists of a sheet (or sheets) of lead so formed as to permit a coating of spongy elemental lead to be held upon the surface exposed to the electrolyte. The positive terminal is constructed similarly and consists of grids of lead

packed with lead dioxide (PbO_2). During discharge, the cell reactions are

$$\begin{aligned}
(-)\ \text{Terminal:}&\quad Pb^0 - 2e^- \rightarrow Pb^{++}\\
(+)\ \text{Terminal:}&\quad \overset{IV+}{Pb} + 2e^- \rightarrow Pb^{++}\\
\hline
\text{Battery:}&\quad Pb^0 + \overset{IV+}{Pb} \rightarrow 2Pb^{++}
\end{aligned}$$

However, since these reactions occur in the presence of sulfuric acid, the lead ions resulting from the primary reactions indicated above are converted to insoluble lead sulfate. Accordingly, the complete

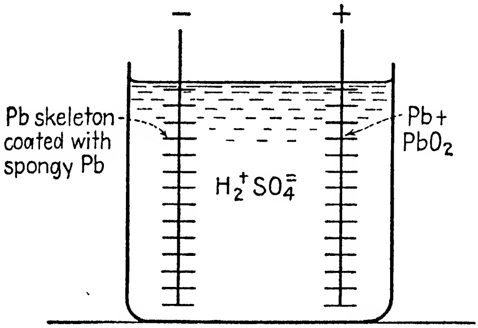


Fig. 110.—Lead storage battery.

description of the process of discharge is represented by the following equation:

$$\underline{Pb^\circ} + \underline{PbO_2} + 2H_2^+SO_4^= \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \underline{2PbSO_4} + 2H_2O$$

As the battery delivers current, the forward reaction results in using up some of the available $H_2^+SO_4^=$ and in the formation of water which dilutes the remaining sulfuric acid. Consequently, the process of discharge is accompanied by a decrease in the specific gravity of the electrolyte, and this is the basis of the test usually applied to determine the condition of a storage battery. Ordinarily, a storage battery should be charged when the specific gravity of the electrolyte decreases to a value in the neighborhood of 1.100.

During discharge, both electrodes become coated with insoluble lead sulfate and, if this coating is allowed to become excessive, the lead sulfate will interfere mechanically with further reaction. Of course, this deposit of lead sulfate is removed during the charging process, which involves the reversal of the reactions that occur during discharge. The lead storage battery is usually charged by connecting it to a 6-volt d.c. source. The ensuing electrolysis not only results in the dissolving of the lead sulfate and the restoration of the initial specific

gravity of the electrolyte but also regenerates spongy lead on the one electrode and lead oxide at the other. At the same time, electrolysis results (to a limited extent) in the discharge of hydrogen and hydroxyl ions with liberation of hydrogen and oxygen. Consequently, water thus lost by electrolysis as well as that lost by evaporation must be replaced periodically by addition of pure water in order to maintain the proper concentration of the electrolyte. When completely charged, the lead storage cell delivers a voltage of about 2.1. An ordinary 6-volt lead storage battery consists of a combination of three such units.

23.7. Edison Storage Cell

Another example of a practical battery, but one less commonly used, is the Edison cell. The active electrode materials consist of iron and nickel dioxide in contact with an electrolyte consisting of aqueous potassium hydroxide solution. Owing to its marked instability, the NiO_2 changes spontaneously to Ni_2O_3 with liberation of oxygen. The reactions responsible for the flow of current are

$$
\begin{array}{rl}
(-)\ \text{Terminal:} & \text{Fe}^{0} - 2e^{-} \rightarrow \text{Fe}^{++} \\
(+)\ \text{Terminal:} & \overset{\text{III+}}{2\text{Ni}} + 2e^{-} \rightarrow \overset{\text{II+}}{2\text{Ni}} \\
\hline
\text{Battery:} & \text{Fe}^{0} + \overset{\text{III+}}{2\text{Ni}} \rightarrow \text{Fe}^{++} + \overset{\text{II+}}{2\text{Ni}}
\end{array}
$$

In the presence of potassium hydroxide, however, the insoluble hydroxides of iron and nickel are produced. The processes of discharge and charge may be represented as follows:

$$\underline{\text{Fe}^{0}} + \underline{\text{Ni}_2\text{O}_3} + 3\text{H}_2\text{O} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \underline{\text{Fe(OH)}_2} + \underline{2\text{Ni(OH)}_2}$$

23.8. Dry Cell

Perhaps the most familiar application of the dry cell is its use in flashlights. This battery (Fig. 111) consists of a zinc case which serves as the negative terminal. The inner walls are covered with a thin coating of porous paper or cloth which keeps the zinc from coming into direct contact with the contents of the cell. A carbon rod placed in the center of the cell constitutes the positive terminal while the remaining space is filled with a pasty mass consisting of a mixture of ammonium chloride and manganese dioxide together with a small amount of zinc chloride. The cell is closed at the top by a coating of pitch or wax which prevents evaporation of water from the moist electrolyte and which also prevents escape of any gases produced within the cell.

The *primary* reactions that occur during discharge are

$$
\begin{aligned}
(-)\ \text{Terminal:}\quad & Zn^{\circ} - 2e^{-} \rightarrow Zn^{++} \\
(+)\ \text{Terminal:}\quad & 2NH_4^{+} + 2e^{-} \rightarrow 2NH_3 + H_2 \\
\hline
\text{Battery:}\quad & Zn^{\circ} + 2NH_4^{+} \rightarrow Zn^{++} + 2NH_3 + H_2
\end{aligned}
$$

Since the gases, NH_3 and H_2, cannot escape, they must be utilized in reactions within the cell. Ammonia molecules combine with zinc ions (produced at the negative terminal) to form the complex ion $[Zn(NH_3)_4]^{++}Cl_2^{-}$. The hydrogen is consumed by reaction with manganese dioxide,

$$\underline{2MnO_2} + H_2 \rightarrow \underline{Mn_2O_3} + H_2O$$

in a *slow* reaction. If a dry cell is used continuously for an appreciable period of time, the foregoing reaction is so slow that the hydrogen is not utilized so rapidly as it is formed. Consequently, gaseous hydrogen collects on the surface of the carbon rod and thus tends to insulate the positive terminal to such an extent that ammonium ions are less readily able to approach the surface of the carbon rod. This results in a decrease in the voltage delivered by the cell. However, if a period of rest is permitted, the accumulated hydrogen is removed slowly by reaction with manganese dioxide and the interference by gaseous hydrogen is thereby eliminated.

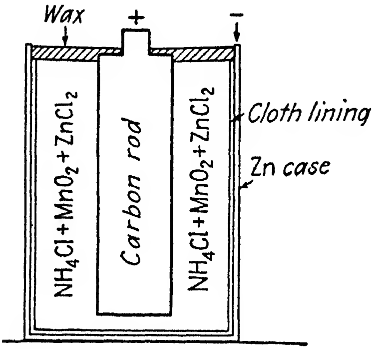


FIG. 111.—Dry cell.

The best commercial dry cells have a rating of about 1.5 volts, and such batteries may not be charged conveniently. The dry cell is rather different from most common batteries in that it is made up largely of solid materials.

EXERCISES

1. Define the following terms: (*a*) negative terminal, (*b*) positive terminal.

2. In the construction of battery cells, why is it not necessary to use materials prepared by electrolysis?

3. If copper and a metal such as cadmium are to be used as electrodes in a battery, why must copper be the positive terminal?

4. What requirement must be met by each of the half cells that together constitute a battery?

5. In terms of the equilibrium existing between an electrode and its surrounding ionic environment, show how the potential of the electrode is dependent upon the ionic concentration.

6. Why must the two solutions surrounding the two electrodes be connected before the battery can deliver current?

7. Write equations for the reactions that occur in (*a*) the lead storage battery, (*b*) the Daniell cell, (*c*) the Edison cell, (*d*) the dry cell.

8. Write equations for the reactions that would occur during the *discharge* of batteries employing the electrode materials listed below. In each case, indicate clearly which reaction occurs at the negative and which at the positive terminal: (*a*) manganese and tin, (*b*) cadmium and bismuth, (*c*) copper and platinum, (*d*) chromium and silver.

9. By reference to Table 26, calculate the voltage that would be produced by each of the batteries suggested in Exercise 8.

10. With regard to the lead storage battery: (*a*) What is the single greatest advantage possessed by this in comparison with other storage batteries? (*b*) Why is it frequently necessary to add pure water to this battery? (*c*) What reasons might one advance in order to explain the fact that such a battery may not be used indefinitely?

11. If a potential of -0.557 volt represents the magnitude of the tendency for a chromium electrode to lose electrons, why is it that a battery involving one chromium terminal has a voltage different from the above value?

12. List the factors that should be taken into consideration if one wishes to construct a practical battery.

13. What is the function of the manganese dioxide used in the dry cell?

14. With reference to batteries in general, what term could be used in place of the term charge?

15. What one factor would seem most likely responsible for the limited useful life of the common dry cell?

16. Represent the reaction between manganese dioxide and hydrogen as a typical oxidation-reduction reaction.

SUGGESTED READING

Journal of Chemical Education

BROCKMAN, The Origin of Voltaic Electricity, 5, 549 (1928); 6, 1293 (1929).
BROCKMAN, Primary Cells—An Historical Sketch, 4, 770 (1927).
REINMUTH, Primary Cells, **6**, 117 (1929).
VOSBURGH and DERR, The Preparation of Weston Standard Cells, **18**, 87 (1941).

Industrial and Engineering Chemistry

REINHARDT, The Automotive Storage Battery, **19**, 1124 (1927).

CHAPTER XXIV

OXIDATION AND REDUCTION

In an earlier discussion relating to various broad types of chemical reactions (Chap. XVIII) the more elementary aspects of oxidation-reduction reactions were considered. Before attempting any more detailed study of this type of chemical change, it is strongly recommended that the student review thoroughly those sections of Chap. XVIII which are concerned with oxidation and reduction. In doing this, particular attention should be directed to definitions of terms, characteristics of oxidation-reduction reactions, and suggested conventional practices employed in the systematic writing of equations representing reactions involving both ionic and covalent compounds.

Particularly in connection with the study of qualitative and quantitative chemical analysis, the student will have need for a considerably more thorough knowledge of oxidation and reduction than may be had by the study of the preceding treatment of the subject. Accordingly, the following section will be concerned with the study of a number of additional examples of commonly encountered oxidation-reduction changes. For the most part, this study will be restricted to cases in which (*a*) the reducing agent consists of a metal and (*b*) the oxidizing agent is a water-soluble ternary compound.

24.1. States of Oxidation and Reduction

Since, for example, sulfur is in periodic group VI and the outermost orbit of the sulfur atom contains 6 electrons, the normal state of the neutral sulfur atom may be represented by the symbol, S^0. It will also be recalled that the normal reaction tendency exhibited by this sulfur atom is that toward gain of 2 electrons. This *reduction* may occur in two stages in each of which 1 electron is gained, *i.e.*,

$$S^0 + 1e^- \rightarrow S^-$$
$$S^- + 1e^- \rightarrow S^=$$

The divalent negative sulfide ion, $S^=$, represents the maximum extent to which sulfur may be reduced, since by gaining 2 electrons, the sulfur atom thereby achieves a structure most closely approaching that of the nearest inert gas. Hence, it is proper to look upon sulfur (or

any other element) as being capable of existing in different conditions or states of reduction. In considering the sequence of changes,

$$S^0 \rightarrow S^- \rightarrow S^=$$

three states of reduction are illustrated, and S^- is said to be more highly reduced than S^0; while $S^=$ may be said to be more highly reduced than either S^0 or S^-.

On the other hand, S^- may be said to represent a higher state of *oxidation* than $S^=$, since, in order to accomplish the change from $S^=$ to S^-, loss of an electron (oxidation) must occur. Similarly, S^0 would be said to be more highly oxidized than either S^- or $S^=$. On the assumption that a divalent negative sulfide ion may lose 2 electrons and thus be converted into a neutral sulfur atom, it must next be recognized that this neutral atom may *lose* successively the 6 electrons in its outermost orbit. Hence, it would appear that the highest possible state of oxidation would be represented by the symbol $\overset{\text{VI}+}{\text{S}}$. Although the independent existence of a positive hexavalent form of sulfur may not be anticipated, one should expect to encounter compounds in which sulfur exhibits an *apparent* positive valence of six, *e.g.*, SO_3. Thus it is seen that an element may exist in a considerable number of different states of oxidation or reduction, and one should learn early to speak in these terms with full understanding of their implications. For practice in the application of these concepts, the student is referred to the exercises at the end of this chapter.

24.2. Factors That Influence the Extent of Oxidation and Reduction

If it is true that an element in a particular state of oxidation may either gain one or more electrons and thus proceed to successively higher states of reduction (lower states of oxidation) *or* lose one or more electrons and thereby proceed into successively higher states of oxidation (lower states of reduction), there arise at once the conjoint problems of the factors that influence the extent of oxidation and reduction and one's ability to exercise control over oxidation-reduction reactions through the medium of these factors. If, upon bringing together an oxidizing agent and a reducing agent, two or more reactions are possible, the predominant reaction will be that which proceeds at the greatest rate under the particular experimental conditions employed. Consequently, since the relative rates of competitive reactions are involved, oxidation-reduction reactions are subject to influence by the same factors that have bearing upon the rates of chemical reactions in general, *viz.*, temperature, concentration, and catalysis. In addition,

the extent of oxidation and reduction is governed largely by the inherent characteristics of the particular oxidizing and reducing agents concerned. This fact may be illustrated best by consideration of a specific case.

Suppose that a metal, *M*, is to be oxidized to M^+ by its reaction with concentrated sulfuric acid at room temperature and in the absence of any catalytic effects. In H_2SO_4, sulfur has an apparent positive valence of 6 and it is recognized that this $\overset{\text{VI+}}{\text{S}}$ might be reduced to $\overset{\text{V+}}{\text{S}}$, $\overset{\text{IV+}}{\text{S}}$, $\overset{\text{III+}}{\text{S}}$, $\overset{\text{II+}}{\text{S}}$, S^+, S^0, S^-, or $S^=$. Of this wide variety of products, that which will be formed or at least that which will predominate if a mixture of products is realized will be determined by the relative effectiveness of *M* as a reducing agent. The effectiveness or "strength" of any reducing agent is dependent upon its inherent tendency toward loss of electrons. Suppose that the metal *M* is one included in Table 26 of Chap. XXIII. If *M* is a metal located near the top of the list, it will have a marked tendency toward loss of electrons, and it may be said to be a strong reducing agent. In its reaction with concentrated sulfuric acid, it would be expected to reduce $\overset{\text{VI+}}{\text{S}}$ to a relatively low state of oxidation. The lower the metal *M* is listed in the table, the less extensive will be the reduction realized when that metal is oxidized by concentrated sulfuric acid. Should the reducing agent be something other than a metal and therefore not listed in Table 26, one could estimate its relative strength by reference to more complete tabulations which include not only the metals but also the nonmetals, their compounds, and ions.

Having seen something of the factors that influence oxidation-reduction changes, attention should next be directed toward the study of specific reactions involving some of the more common oxidizing and reducing agents.

24.3. Reactions of Concentrated Sulfuric Acid

The student has already learned that the reactions of dilute sulfuric acid are those dependent upon the existence of hydrogen ions, or rather hydronium ions, in the water solutions.

$$H_2^+SO_4^= + H_2O \rightarrow H_3O^+ + HSO_4^-$$

Since concentrated sulfuric acid contains relatively little water (if, indeed any is present at all), reactions requiring the presence of hydronium ions are either suppressed or eliminated entirely. Consequently, the most common reactions of the concentrated acid are those which are concerned primarily with the central sulfur atom which has

an apparent positive valence of six and not with ions resulting from interaction of the solute with the solvent.

Concentrated sulfuric acid is a very effective oxidizing agent. More properly, one should say that the central sulfur atom in H_2SO_4 is an effective oxidizing agent since it is this atom which acts as the electron acceptor. Accordingly, when concentrated sulfuric acid participates in an oxidation-reduction reaction, reduction of $\overset{\text{VI+}}{\text{S}}$ occurs in a degree dependent upon the strength of the reducing agent employed. These reactions are of interest here not only because of the manner in which they illustrate oxidation-reduction processes but also because certain of the final products of these reactions are important and useful commercial chemicals. Some of the more common reduction products of concentrated sulfuric acid are listed in Table 27.

TABLE 27
REDUCTION PRODUCTS OF CONCENTRATED SULFURIC ACID

	Electrons gained by $\overset{\text{VI+}}{\text{S}}$	Reduction products	
		Apparent valence of S	Examples
$H_2\overset{\text{VI+}}{\text{S}}O_4$	2	IV+	Sulfur dioxide* (SO_2)
	3	III+	Hyposulfurous acid† ($H_2S_2O_4$)
	6	0	Elemental sulfur (S^0)
	8	II−	Hydrogen sulfide‡ (H_2S)

* Other examples include sulfurous acid and its salts.
† Or salts of this acid.
‡ Or any salt of hydrosulfuric acid.

If one wished to reduce concentrated sulfuric acid to sulfurous acid, it is apparent from Table 27 that, since only the gain of 2 electrons is required, this change should be accomplished by use of a relatively weak reducing agent, *e.g.*, the metal copper (see Table 26, Chap. XXIII). In this reaction copper is oxidized (loses electrons) and the change may be represented as follows:

$$(a)\qquad Cu^0 - 2e^- \rightarrow Cu^{++}$$

$$(b)\qquad \overset{\text{VI+}}{\text{S}} + 2e^- \rightarrow \overset{\text{IV+}}{\text{S}}$$

$$(c)\qquad Cu^0 + \overset{\text{VI+}}{\text{S}} \rightarrow Cu^{++} + \overset{\text{IV+}}{\text{S}}$$

Having represented the essential oxidation-reduction changes [equations (*a*) and (*b*)] together with their summation in equation (*c*), one may next proceed to write the more complete and conventional type

of chemical equation in a manner wholly analogous to that previously outlined in Chap. XVIII. Recognizing that the $\overset{VI+}{S}$ was used in the form of H_2SO_4 and that the product containing $\overset{IV+}{S}$ is sulfurous acid, one may modify equation (*c*) by incorporation of this information, thus,

$$Cu^0 + H_2SO_4 \rightarrow Cu^{++} + H_2SO_3$$

From this *unbalanced* expression, students are frequently led to suggest that copper oxide (CuO) is formed in the reaction since, by representing this product, the above expression may be balanced. However, copper oxide reacts with sulfuric acid; hence this suggestion must be rejected. As a matter of fact undoubtedly already acquired by the student's experience in the laboratory, the reaction between copper and an excess of sulfuric acid results in the formation of copper sulfate. [In this connection, it should be recalled that a reaction between an oxidizing acid and a metal listed below hydrogen in the order of activity of metals (Sec. 8.2) results in the production of a *salt* and products other than hydrogen.] Consequently, equation (*c*) leads finally to a complete equation.

$$(d) \qquad Cu^0 + H_2SO_4 + H_2^+SO_4^= \rightarrow Cu^{++}SO_4^= + H_2SO_3 + H_2O$$

The formula for sulfuric acid is represented twice only for the purpose of emphasizing the fact that one molecule acts as an oxidizing agent and actually participates in the fundamental oxidation-reduction change whereas the other molecule merely behaves as a strong electrolyte and supplies the sulfate ion required for the formation of copper sulfate. When equations of this sort are written, the various steps should, of course, be assembled in the following form:

$$\begin{array}{ll}
(a) & Cu^0 - 2e^- \rightarrow Cu^{++} \\
(b) & \overset{VI+}{S} + 2e^- \rightarrow \overset{IV+}{S} \\
\hline
(c) & Cu^0 + \overset{VI+}{S} \rightarrow Cu^{++} + \overset{IV+}{S} \\
(d) & Cu^0 + H_2SO_4 + H_2^+SO_4^= \rightarrow Cu^{++}SO_4^= + H_2SO_3 + H_2O
\end{array}$$

Should one wish to produce elemental sulfur by the reduction of sulfuric acid, it is apparent at once that, since the gain of 6 electrons is involved, this reduction process will require a reducing agent stronger than was required in the production of sulfurous acid. Thus, copper would prove to be inadequate and one would have to use a metal such as lead, *i.e.*, one listed higher in Table 26. The final equation representing this reaction may be developed as follows:

$$
\begin{array}{ll}
(a) & 3Pb^0 - 6e^- \rightarrow 3Pb^{++} \\
(b) & \overset{VI+}{S} + 6e^- \rightarrow S^\circ \\
(c) & 3Pb^0 + \overset{VI+}{S} \rightarrow 3Pb^{++} + S^\circ \\
(d) & \underline{3Pb^0} + H_2SO_4 + 3H_2^+SO_4^= \rightarrow \underline{3Pb^{++}SO_4^=} + \underline{S^0} + 4H_2O
\end{array}
$$

An example of a reaction involving concentrated sulfuric acid and a strong reducing agent is provided by that in which Zn^0 is oxidized to Zn^{++}. In this case, the reducing agent is a sufficiently effective electron donor to permit the gain of 8 electrons, thus reducing $\overset{VI+}{S}$ to $\overset{II-}{S}$, as shown in detail by the following equations:

$$
\begin{array}{ll}
(a) & 4Zn^0 - 8e^- \rightarrow 4Zn^{++} \\
(b) & \overset{VI+}{S} + 8e^- \rightarrow \overset{II-}{S} \\
(c) & 4Zn^0 + \overset{VI+}{S} \rightarrow 4Zn^{++} + \overset{II-}{S} \\
(d) & \underline{4Zn^0} + H_2SO_4 + 4H_2^+SO_4^= \rightarrow 4Zn^{++}SO_4^= + \overline{H_2S} + H_2O
\end{array}
$$

The reactions illustrated by the foregoing examples represent the most common behaviors exhibited by concentrated sulfuric acid in its oxidation-reduction reactions with metals. Of course, $\overset{VI+}{S}$ may also be reduced to other states of oxidation by the judicious selection of the reducing agent. It should be recognized also that reducing agents other than the metals may be employed. For example, ferrous sulfate reduces concentrated sulfuric acid to sulfur dioxide. Since ferrous sulfate is the reducing agent (and must therefore be oxidized), one would anticipate that ferric sulfate would be the oxidation product.

$$
\begin{array}{ll}
(a) & 2Fe^{++} - 2e^- \rightarrow 2Fe^{+++} \\
(b) & \overset{VI+}{S} + 2e^- \rightarrow \overset{IV+}{S} \\
(c) & 2Fe^{++} + \overset{VI+}{S} \rightarrow 2Fe^{+++} + \overset{IV+}{S} \\
(d) & 2FeSO_4 + H_2SO_4 + H_2^+SO_4^= \rightarrow Fe_2^{+++}(SO_4)_3^= + \overline{SO_2} + 2H_2O
\end{array}
$$

Other reactions of this character are included among the exercises at the end of this chapter.

24.4. Oxidation by Nitric Acid

Because nitric acid and concentrated sulfuric acid are those most extensively used as oxidizing acids, it is instructive to compare these two acids in relation to their behavior in oxidation-reduction reactions. Two essential differences are to be recognized. First, although sulfuric acid behaves as an oxidizing agent only when *concentrated*, nitric acid serves as an oxidizing agent at any concentration—even when extremely dilute. Second, whereas the nature of the reduction prod-

ucts of sulfuric acid is dependent only upon the strength of the reducing agent, *the nature of the products that are formed by the reduction of nitric acid depends upon both the strength of the reducing agent and the concentration of the acid.*

The apparent valence of nitrogen in HNO_3 is V^+, a fact that is in accord with the position of nitrogen in the periodic arrangement of the elements. Consequently, the use of nitric acid as an oxidizing agent might be expected to result in the gain (by $\overset{V+}{N}$) of 1, 2, 3, 4, or 5 electrons, the latter resulting in the formation of elemental nitrogen. With this degree of reduction accomplished, the normal nitrogen atom having 5 electrons in its outermost orbit would tend to gain an additional 1, 2, or 3 electrons. Hence, numerous states of oxidation (or reduction) of nitrogen may be realized through oxidation-reduction reactions involving nitric acid. The various common reduction products are summarized in Table 28. In view of the considerable number of reduction products, it becomes necessary next to study in detail the conditions that permit the formation of these several compounds in which nitrogen exists in different states of oxidation.

Influence of Strength of the Reducing Agent. Just as was done in connection with the study of reactions of concentrated sulfuric

TABLE 28

REDUCTION PRODUCTS OF NITRIC ACID

	Electrons gained by $\overset{V+}{N}$	Reduction products	
		Apparent valence of N	Examples
$H\overset{V+}{N}O_3$	1	IV+	Nitrogen dioxide (NO_2)
	2	III+	Nitrous acid* (HNO_2)
	3	II+	Nitric oxide (NO)
	4	I+	Nitrous oxide (N_2O)
	5	0	Elemental nitrogen (N_2)
	6	I−	Hydroxylamine (NH_2OH)
	7	II−	Hydrazine (N_2H_4)
	8	III−	Ammonia (NH_3)

* Or salts of this acid, *e.g.*, sodium nitrite ($NaNO_2$).

acid, one may select three metals for use as reducing agents of markedly different strength. Thus, Cu, Pb, and Zn, may be chosen to represent weak, intermediate, and strong reducing agents, respectively. In their reactions with nitric acid, the extent to which each metal (reducing agent) will serve to reduce $\overset{V+}{N}$ depends upon the relative tendency

that the metal exhibits toward loss of electrons (see Table 26, Chap. XXIII). If, for example, *concentrated* nitric acid is reduced by copper, it is found that the weak reducing action of this metal is sufficient only to reduce $\overset{V+}{N}$ to $\overset{IV+}{N}$, with the resulting formation of nitrogen dioxide as shown by the following equations:

$$
\begin{array}{ll}
(a) & Cu^0 - 2e^- \rightarrow Cu^{++} \\
(b) & 2\overset{V+}{N} + 2e^- \rightarrow 2\overset{IV+}{N} \\
\hline
(c) & Cu^0 + 2\overset{V+}{N} \rightarrow Cu^{++} + 2\overset{IV+}{N} \\
(d) & \underline{Cu^0} + 2HNO_3 + 2H^+NO_3^- \rightarrow Cu^{++}(NO_3)_2^- + 2\overline{NO_2} + 2H_2O
\end{array}
$$

If, on the other hand, one should use lead as the reducing agent, its greater effectiveness as an electron donor (reducing agent) permits reduction of $\overset{V+}{N}$ to $\overset{III+}{N}$ or, in other words, reduction of HNO_3 to HNO_2, thus,

$$
\begin{array}{ll}
(a) & Pb^0 - 2e^- \rightarrow Pb^{++} \\
(b) & \overset{V+}{N} + 2e^- \rightarrow \overset{III+}{N} \\
\hline
(c) & Pb^0 + \overset{V+}{N} \rightarrow Pb^{++} + \overset{III+}{N} \\
(d) & Pb^0 + HNO_3 + 2H^+NO_3^- \rightarrow Pb^{++}(NO_3)_2^- + HNO_2 + H_2O
\end{array}
$$

Finally, the use of the strong reducing agent, zinc, is found to result in the reduction of HNO_3 to NO (*i.e.*, from $\overset{V+}{N}$ to $\overset{II+}{N}$), in accordance with the following equations:

$$
\begin{array}{ll}
(a) & 3Zn^0 - 6e^- \rightarrow 3Zn^{++} \\
(b) & 2\overset{V+}{N} + 6e^- \rightarrow 2\overset{II+}{N} \\
\hline
(c) & 3Zn^0 + 2\overset{V+}{N} \rightarrow 3Zn^{++} + 2\overset{II+}{N} \\
(d) & \underline{3Zn^0} + 2HNO_3 + 6H^+NO_3^- \rightarrow 3Zn^{++}(NO_3)_2^- + 2\overline{NO} + 4H_2O
\end{array}
$$

From these examples, it is apparent that even the use of zinc for the reduction of concentrated nitric acid results in a reaction in which only 3 electrons are gained by $\overset{V+}{N}$. Since it is assumed in this discussion that zinc typifies the strong reducing agents, it follows that more extensive reduction of nitric acid must be brought about, not by the use of stronger reducing agents, but rather by using something other than the concentrated acid.

Influence of Concentration of the Acid. If one continues to use Cu, Pb, and Zn as examples of weak, intermediate, and strong reducing agents and investigates their reactions with *dilute* nitric acid, it is found that reduction in each case will be correspond-

ingly greater than was realized in using the concentrated acid. Thus, copper and dilute nitric acid react to form nitric oxide, thus,

$$\text{(a)} \quad 3Cu^0 - 6e^- \rightarrow 3Cu^{++}$$

$$\text{(b)} \quad 2\overset{V+}{N} + 6e^- \rightarrow 2\overset{II+}{N}$$

$$\text{(c)} \quad 3Cu^0 + 2\overset{V+}{N} \rightarrow 3Cu^{++} + 2\overset{II+}{N}$$

$$\text{(d)} \quad \underline{3Cu^0} + 2HNO_3 + 6H^+NO_3^- \rightarrow 3Cu^{++}(NO_3)_2^- + 2\overline{NO} + 4H_2O$$

Perhaps this is the best possible example of the influence of concentration. With dilute nitric acid, the weak reducing agent, Cu, produces the same *extent* of reduction as is realized when the strong reducing agent, Zn, reacts with the concentrated acid. Hence, dilution of the acid must render the $\overset{V+}{N}$ more readily capable of acting as an electron acceptor (oxidizing agent). Continuation of this trend is seen when one studies the interaction of lead and dilute nitric acid. When the concentrated acid was employed, only 2 electrons were gained by $\overset{V+}{N}$ whereas with the dilute acid, 4 electrons are gained in the reduction of HNO_3 to N_2O.

$$\text{(a)} \quad 4Pb^0 - 8e^- \rightarrow 4Pb^{++}$$

$$\text{(b)} \quad 2\overset{V+}{N} + 8e^- \rightarrow 2\overset{I+}{N}$$

$$\text{(c)} \quad 4Pb^0 + 2\overset{V+}{N} \rightarrow 4Pb^{++} + 2\overset{I+}{N}$$

$$\text{(d)} \quad \underline{4Pb^0} + 2HNO_3 + 8H^+NO_3^- \rightarrow 4Pb^{++}(NO_3)_2^- + \overline{N_2O} + 5H_2O$$

Still more extensive reduction would be expected if one reduced dilute nitric acid by means of the strong reducing agent, zinc. As shown in Table 29, this prediction is realized since elemental nitrogen is found to be the reduction product. The summary provided by Table 29 calls attention to the fact that still more extensive reduction results from the use of *very dilute* acid. Of the three products indicated, only the formation of ammonia is of sufficient importance to warrant further comment. In this reaction, $\overset{V+}{N}$ is best used not in the form of nitric acid but rather as a salt such as $NaNO_3$ (in the presence of an excess of aqueous sodium hydroxide solution), from which the formation of ammonia occurs in accordance with the following equations:

$$\text{(a)} \quad 4Zn^0 - 8e^- \rightarrow 4\overset{II+}{Zn}$$

$$\text{(b)} \quad \overset{V+}{N} + 8e^- \rightarrow \overset{III-}{N}$$

$$\text{(c)} \quad 4Zn^0 + N \rightarrow 4\overset{II+}{Zn} + \overset{III-}{N}$$

$$\text{(d)} \quad \underline{4Zn^0} + NaNO_3 + 3Na^+OH^- + 2H_2O \rightarrow 4Na^+(HZnO_2)^- + \overline{NH_3}$$

TABLE 29

VARIATIONS IN PRODUCTS OBTAINED BY THE REDUCTION OF NITRIC ACID

Concentration of $H\overset{\text{V+}}{N}O_3$	Reducing agent	Electrons gained by $\overset{\text{V+}}{N}$	Apparent valence of N in product	Predominant product
Concentrated.	Cu	1	$\overset{\text{IV+}}{N}$	Nitrogen dioxide (NO_2)
	Pb	2	$\overset{\text{III+}}{N}$	Nitrous acid (HNO_2)
	Zn	3	$\overset{\text{II+}}{N}$	Nitric oxide (NO)
Dilute.	Cu	3	$\overset{\text{II+}}{N}$	Nitric oxide (NO)
	Pb	4	$\overset{\text{I-}}{N}$	Nitrous oxide (N_2O)
	Zn	5	N^0	Nitrogen (N_2)
Very dilute.	Cu	6	$\overset{\text{I-}}{N}$	Hydroxylamine (NH_2OH)
	Pb	7	$\overset{\text{II-}}{N}$	Hydrazine (N_2H_4)
	Zn	8	$\overset{\text{III-}}{N}$	Ammonia (NH_3)

This case illustrates the reduction of $\overset{\text{V+}}{N}$ to its lowest state of oxidation, *viz.*, $\overset{\text{III-}}{N}$ as exemplified by ammonia.

Formation of Mixtures. Throughout the preceding discussion it has been implied (for purposes of simplification) that in each reaction involving concentrated sulfuric acid and nitric acid, a single reduction product is obtained. A little reflection, however, leads to the conclusion that this will occur only under very carefully controlled experimental conditions. Mixtures may be formed owing to (*a*) changes in the concentration of the acid or (*b*) the specific properties of the reducing agent. Reference to Table 26 will show that there are numerous metals between copper and lead. If, for example, concentrated nitric acid were reduced by cadmium, a mixture of nitrous acid and nitric acid would probably result. Similarly, mixtures might also be formed by the reduction of concentrated sulfuric acid by means of certain reducing agents. It should also be recognized that, particularly in the case of nitric acid, the usual practice involves addition of the reducing agent to an excess of the acid. In the subsequent oxidation-reduction reaction, the acid becomes progressively more dilute owing to utilization of some of the acid and dilution resulting from the formation of water as a product of the reaction. Hence, if one added zinc to con-

centrated nitric acid, the progressive dilution of the acid solution would result in the formation of reduction products other than nitric oxide. Of course, one might avoid these complications by adding the concentrated acid to the zinc in an apparatus so designed that the metal is exposed only to the concentrated acid, but such experimental conditions are certainly not common to reactions of this type.

In consequence of the factors indicated above, one should emphasize *the predominant reduction product* rather than *the* reduction product. In the great majority of cases in which several reduction products are possible, mixtures will usually result unless special precautions are exercised.

24.5. Predictions Relative to the Occurrence of Oxidation-reduction Reactions

Having seen that it is possible to predict whether metathetical reactions will occur and go essentially to completion, one is confronted by the question as to whether similar predictions are possible in the case of oxidation-reduction reactions. It is at once apparent that this problem is complicated by the facts (*a*) that one must have a means of deciding which of a number of possible products will actually be formed and (*b*) that the nature of the products often is influenced by changes in temperature, concentration, and relative strength of the oxidizing and reducing agents.

One may make certain forecasts solely on the basis of information such as that given in Table 26, Chap. XVIII, but even so one must recognize that the data contained therein relate to only one temperature and one concentration. For example, one would predict that, if iron metal is added to a 1 M solution of copper sulfate, copper would be displaced by iron owing to its greater tendency to lose electrons and exist in the ionic condition.

$$(a) \qquad Fe^0 - 2e^- \rightarrow Fe^{++}$$

$$(b) \qquad Cu^{++} + 2e^- \rightarrow Cu^0$$

$$(c) \qquad Fe^0 + Cu^{++} \rightarrow Fe^{++} + Cu^0$$

$$(d) \qquad \underline{Fe^0} + Cu^{++}SO_4^{=} \rightarrow Fe^{++}SO_4^{=} + \underline{Cu^0}$$

Similarly, one would predict that iron would displace cadmium from a solution of a soluble cadmium salt, *but at a slower rate*, and that iron would not displace a metal having a greater tendency to lose electrons, *e.g.*, Mn^{++} from $Mn^{++}SO_4^{=}$. Decisions as to what will occur in cases of this sort are of the same type and are made on the same basis as those involved in deciding which of two metals will act as the negative (or positive) terminal of a battery cell (Sec. 23.2).

It must be pointed out, however, that the data of Table 26 are quite limited in scope since only the metals are included. If a more elaborate scheme of prediction were to be used, it would be necessary to have far more extensive data tabulated similarly and including the nonmetals in their various states of oxidation, as well as much more extensive data relating to other oxidation states of the metals. Schemes of prediction based on data of this character have been devised and references thereto are given at the end of this chapter.

24.6. Common Oxidizing and Reducing Agents

Aside from the use of metals as reducing agents and the use of nitric and concentrated sulfuric acids as oxidizing agents, there are many common substances that are useful in oxidation-reduction chemistry. Many of these reactions are of importance in the various aspects of analytical chemistry. In Table 30, there are included numerous examples and in each case, the *most common* valence change is indicated. For example, $\overset{\text{VI+}}{\text{Cr}}$ in $K_2Cr_2O_7$ may under suitable conditions be reduced to several lower states of oxidation, but the change from $\overset{\text{VI+}}{\text{Cr}}$ to Cr^{+++} is that most commonly encountered.

TABLE 30
COMMON OXIDIZING AGENTS

Oxidizing agents		Reduction products*	
Name	Formula	Name	Formula
Stannic chloride	$SnCl_4$	Stannous chloride	$SnCl_2$
Mercuric chloride	$HgCl_2$	Mercurous chloride	Hg_2Cl_2
Potassium permanganate	$KMnO_4$	Manganous nitrate†	$Mn(NO_3)_2$
		Manganese dioxide‡	MnO_2
Ceric sulfate	$Ce(SO_4)_2$	Cerous sulfate	$Ce_2(SO_4)_3$
Ferric sulfate	$Fe_2(SO_4)_3$	Ferrous sulfate	$FeSO_4$
Potassium dichromate	$K_2Cr_2O_7$	Chromic chloride	$CrCl_3$
Sodium arsenate	Na_3AsO_4	Sodium arsenite	Na_3AsO_3
Sodium tetrathionate	$Na_2S_4O_6$	Sodium thiosulfate	$Na_2S_2O_3$
Potassium perchlorate	$KClO_4$	Potassium chlorate	$KClO_3$
Sodium bismuthate	$NaBiO_3$	Bismuth nitrate	$Bi(NO_3)_3$

* A number of the reduction products listed are commonly useful as *reducing agents*, *e.g.*, $SnCl_2$, $Ce_2(SO_4)_3$, $FeSO_4$, $Na_2S_2O_3$, etc.
† From reaction in acidic solution.
‡ From reaction in basic solution.

Since, according to Table 30, mercuric chloride is an oxidizing agent and stannous chloride is a reducing agent, one would anticipate that the following reaction would occur:

$$\begin{array}{ll}
(a) & Sn^{++} - 2e^- \rightarrow Sn^{++++} \\
(b) & 2\overset{II+}{Hg} + 2e^- \rightarrow 2\overset{I+}{Hg} \\
\hline
(c) & Sn^{++} + 2\overset{II+}{Hg} \rightarrow Sn^{++++} + 2\overset{I+}{Hg} \\
(d) & Sn^{++}Cl_2^- + 2HgCl_2 \rightarrow Sn^{++++}Cl_4^- + \underline{Hg_2Cl_2}
\end{array}$$

In fact, this reaction is widely used in qualitative chemical analysis procedures that involve the subsequent reduction of mercurous chloride to elemental mercury by means of an additional quantity of stannous chloride.

$$\begin{array}{ll}
(a) & Sn^{++} - 2e^- \rightarrow Sn^{++++} \\
(b) & 2\overset{I+}{Hg} + 2e^- \rightarrow 2Hg^\circ \\
\hline
(c) & Sn^{++} + 2\overset{I+}{Hg} \rightarrow Sn^{++++} + 2Hg^\circ \\
(d) & Sn^{++}Cl_2^- + \underline{Hg_2Cl_2} \rightarrow Sn^{++++}Cl_4^- + \underline{2Hg^\circ}
\end{array}$$

Although, as indicated above, stannous chloride is most commonly used as a reducing agent, it should be recognized that in the presence of a still stronger reducing agent, $SnCl_2$ would act as an oxidizing agent and could be reduced to elemental tin.

Other oxidation-reduction reactions that have been found useful in chemical analysis include the oxidation of ferrous sulfate by potassium dichromate,

$$\begin{array}{ll}
(a) & 6Fe^{++} - 6e^- \rightarrow 6Fe^{+++} \\
(b) & 2\overset{VI+}{Cr} + 6e^- \rightarrow 2Cr^{+++} \\
\hline
(c) & 6Fe^{++} + 2\overset{VI+}{Cr} \rightarrow 6Fe^{+++} + 2Cr^{+++} \\
(d) & 6FeSO_4 + K_2Cr_2O_7 + 7H_2^+SO_4^= \rightarrow 3Fe_2^{+++}(SO_4)_3^= + Cr_2^{+++}(SO_4)_3^= + K_2^+SO_4^= \\
 & \qquad + 7H_2O
\end{array}$$

the oxidation of hydrogen sulfide by means of potassium permanganate in acidic solutions,

$$\begin{array}{ll}
(a) & 5S^= - 10e^- \rightarrow 5S^0 \\
(b) & 2\overset{VII+}{Mn} + 10e^- \rightarrow 2Mn^{++} \\
\hline
(c) & 5S^= + 2\overset{VII+}{Mn} \rightarrow 5S^0 + 2Mn^{++} \\
(d) & 5H_2S + 2KMnO_4 + 3H_2^+SO_4^= \rightarrow \underline{5S^0} + 2Mn^{++}SO_4^= + K_2^+SO_4^= + 8H_2O
\end{array}$$

and the oxidation of manganous nitrate to permanganic acid by the use of sodium bismuthate as the oxidizing agent,

$$\begin{array}{ll}
(a) & 2Mn^{++} - 10e^- \rightarrow 2\overset{VII+}{Mn} \\
(b) & 5\overset{V+}{Bi} + 10e^- \rightarrow 5Bi^{+++} \\
\hline
(c) & 2Mn^{++} + 5\overset{V+}{Bi} \rightarrow 2\overset{VII+}{Mn} + 5Bi^{+++} \\
(d) & 2Mn(NO_3)_2 + \underline{5NaBiO_3} + 16H^+NO_3^- \rightarrow 2H^+MnO_4^- + 5Bi^{+++}(NO_3)_3^- \\
 & \qquad + 5Na^+NO_3^- + 7H_2O
\end{array}$$

Other reactions of this general type together with their applications will be encountered by the student of analytical chemistry.

EXERCISES

1. Of the two states of oxidation indicated in each of the following cases, which one represents the higher state of oxidation (*i.e.*, the more highly oxidized form)?

(*a*) S^0 or S^-	(*d*) Pb^{++} or Pb^0
(*b*) Cu^0 or Cu^{++}	(*e*) Pb^{++} or $\overset{IV+}{Pb}$
(*c*) I_2^0 or I^-	(*f*) H_2^0 or H^+

2. If each of the following compounds was to be oxidized by means of a suitable oxidizing agent, (*a*) which element will most likely lose electrons and (*b*) what will be the final state of oxidation of that element?

(*a*) Cu_2Cl_2	(*d*) Na_2S
(*b*) KBr	(*e*) As_2O_3
(*c*) PbO	(*f*) $ZnCl_2$

3. Essentially what is implied when one states that two reducing agents are of different strengths?

4. When sodium iodide is added to an excess of concentrated sulfuric acid, elemental iodine and hydrogen sulfide gas are produced. Write (in steps) the equation for this reaction.

5. Gaseous sulfur dioxide is liberated by the interaction of ferrous sulfate and concentrated sulfuric acid. Write (in steps) the corresponding equations.

6. On the assumption that all of the combined sulfur involved is changed to elemental sulfur, write (in steps) the equation for the reaction between H_2S and concentrated H_2SO_4.

7. Compare the oxidizing action of nitric acid with that of concentrated sulfuric acid.

8. On the basis of the information contained in Tables 26 and 29, what reduction product would predominate if dilute nitric acid were to react with metallic bismuth?

9. Write (in steps) the equation for the reaction between zinc and dilute nitric acid.

10. By means of a suitable diagram, suggest an apparatus in which concentrated nitric acid could be reduced by zinc under such conditions that *only* nitric oxide will be formed as the reduction product.

11. What factors tend to complicate the problem of prediction with regard to the products of many oxidation-reduction reactions?

12. If separate portions of a 1 *M* solution of nickel chloride are treated with bismuth, tin, chromium, and aluminum metals, (*a*) predict whether reaction will occur in each case and (*b*), if reaction is predicted, write (in steps) the equations for these reactions.

13. The reduction of iodine by sodium thiosulfate results in the formation of sodium tetrathionate ($Na_2S_4O_6$). Write (in steps) the equation for this reaction.

14. If copper sulfide is treated with warm dilute nitric acid, the CuS is dissolved and S^0 and gaseous NO are produced. Write (in steps) an equation to represent this change.

15. Write (in steps) an equation showing the formation of sodium thiosulfate by the interaction of sodium sulfite solution and elemental sulfur.

SUGGESTED READING

Journal of Chemical Education

LOCHTE, The Pole Reaction Method of Teaching Oxidation and Reduction Reactions, **4**, 223 (1927).

HALL, Oxidation-reduction Reactions, **6**, 479 (1929).

BRINKLEY, Typical Oxidation-reduction Reactions in General Chemistry, **6**, 1894 (1929).

JETTE and LA MER, The Balancing of Oxidation-reduction Equations, **4**, 1021, 1159 (1927).

LOCHTE, Electromotive Force Table and Oxidation-reduction Reactions, **10**, 373 (1933).

BENNETT, Balancing Equations by the Valence-change Method, **12**, 189 (1935).

MORRIS, The Balancing of Oxidation-reduction Equations, **15**, 538 (1938).

LAWRENCE, Short Cuts in Balancing Oxidation-reduction Equations, **17**, 388 (1940).

CHAPTER XXV

METALS AND ALLOYS

Although no definite line of demarkation can be drawn between the metallic and the nonmetallic elements (Sec. 13.3), approximately three-fourths of the known chemical elements are usually considered to be predominantly metallic in character. The objective of the present discussion is the consideration of certain chemical and physical properties of the metals from the viewpoint of their constituting a class of elements all of which possess certain characteristics in common. Wholly aside from the fact that metals are far more numerous than nonmetals, the many and varied industrial uses of metals imply the importance of an understanding of the properties of the metallic state. Such knowledge has been largely responsible for the development of those industrial applications which have contributed so much to the progress of modern industry.

25.1. Occurrence of Metals

The *availability* of an element (whether metallic or nonmetallic) depends upon both its abundance and its mode of existence in nature. Of two metals on or near the earth's surface one may be far more abundant than the other and yet be far less accessible for the reason that it does not occur in high concentration at any one or more places. In other words, a very abundant element may be relatively inaccessible because it is fairly uniformly distributed throughout the earth's surface. On the other hand, a metal that exists on the earth only to a limited extent may be readily available because the existing supplies are found in rich deposits consisting principally of that metal or one or more of its compounds. These ideas are strikingly illustrated by the comparison of the history of magnesium and lead. Although more than one thousand times more abundant than lead, the extensive commercial utilization of magnesium is a relatively modern development whereas lead was known and used by the Babylonians and the Romans.

Early use of lead, as well as metals such as tin, copper, silver, gold, or mercury, was also possible by virtue of the fact that these metals exist in nature either in the uncombined condition or in forms of chemi-

cal combination from which these metals may be secured by relatively simple procedures.

Regardless of their chemical character, the various forms in which both nonmetals and metals occur in nature are usually called *minerals.* A mineral that is of such a character that it serves as an economical source for the commercial production of a metal or a nonmetal is referred to as an *ore.*

Native Metals. Only a relatively small number of the metals are capable of existence in nature in the uncombined condition, *e.g.*, copper, silver, gold, antimony, bismuth, and platinum. These so-called *noble metals* are those which exhibit such low degrees of chemical activity that they can exist in nature without entering into chemical combinations resulting from reactions with water, atmospheric oxygen, or carbon dioxide.

Types of Ores. In addition to the native metals, which are *relatively* unimportant, a wide variety of minerals is found in nature, and these minerals provide the chief ores from which the various metals are extracted commercially. Although these ores encompass many different types of chemical compounds, the great majority of the more important ores of the metals are notable for their chemical simplicity, as is shown by the following.

1. **Sulfides.** The simple or (less frequently) complex sulfides of a number of heavy metals are employed extensively as sources of these metals. For example, the minerals[1] *chalcocite* (Cu_2S), *chalcopyrite* ($CuFeS_2$), *cinnabar* (HgS), *galena* (PbS), *sphalerite* (ZnS) are typical of the useful sulfide ores of heavy metals.

2. **Oxides.** The minerals *hematite* (Fe_2O_3), *bauxite* ($Al_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot 2H_2O$), *cassiterite* (SnO_2), *pyrolusite* (MnO_2), and *franklinite* ($ZnO \cdot Fe_2O_3$) serve as examples of common oxide ores. Because of their importance as sources of iron and aluminum, oxide ores are perhaps of greater importance than any other single type.

3. **Carbonates.** Among many carbonate minerals that provide the corresponding metals, the basic carbonate *malachite* [$Cu_2(OH)_2CO_3$] and the normal carbonates *siderite* ($FeCO_3$), *cerussite* ($PbCO_3$), *strontianite* ($SrCO_3$), and *dolomite* ($CaCO_3 \cdot MgCO_3$) are representative ores.

[1] The names assigned to minerals have little, if any, significance. These names are not systematic and provide no indication of the chemical character of the substances involved. However, since these trivial names are in common use, it is best that the student become familiar with both the mineral names and the corresponding chemical names. Thus, both the names *cuprous sulfide* and *chalcocite* should be associated with the formula Cu_2S.

4. **Other Types.** Without going into details regarding each type of compound, the minerals listed in Table 31 show the wide variety

TABLE 31
SOME COMMON MINERALS OTHER THAN SULFIDES, OXIDES, AND CARBONATES

Type of compound	Mineral name	Formula	Chemical name
Halogenides.	Rock salt	$NaCl$	Sodium chloride
	Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$	Potassium magnesium chloride hexahydrate
	Sylvite	KCl	Potassium chloride
	Horn silver	$AgCl$	Silver chloride
Sulfates.	Epsomite	$MgSO_4 \cdot 7H_2O$*	Magnesium sulfate heptahydrate
	Barite	$BaSO_4$	Barium sulfate
	Gypsum	$CaSO_4 \cdot 2H_2O$	Calcium sulfate dihydrate
	Anglesite	$PbSO_4$	Lead sulfate
Silicates.	Willemite	Zn_2SiO_4	Zinc orthosilicate
	Asbestos	$CaMg_3Si_4O_{12}$	Calcium magnesium silicate
	Mica	$KAl_3H_2Si_3O_{12}$	Potassium aluminum hydrogen silicate
	Beryl	$Be_3Al_2Si_6O_{18}$	Beryllium aluminum silicate
Miscellaneous . . .	Wolfram	$FeWO_4$	Ferrous tungstate
	Chalcolite	$Cu(UO_2)(PO_4)_2 \cdot 8H_2O$	Copper uranyl phosphate octahydrate
	Chromite	$Fe(CrO_2)_2$	Ferrous chromite
	Crocoite	$PbCrO_4$	Lead chromate

* In the pure condition, this compound is known as *Epsom salt*.

of types of compounds that is known and used. This tabulation is intended to be illustrative rather than exhaustive.

25.2. Extraction of Metals from Their Ores

The science of *metallurgy* is concerned with the extraction of metals from their ores and with the subsequent purification of the metals. Since metals exist in nature in such a wide variety of types of chemical combination, it is apparent that many different kinds of chemical treatment may be required. Other factors that complicate the subject of metallurgy are the varying degrees of chemical activity exhibited by the metals and the fact that both rich and low-grade ores must

be used. Although it is somewhat difficult to generalize with respect to a problem involving so many variables, it is convenient to consider the subject of metallurgy as involving a number of fairly well-defined steps.

Concentration Processes. On the assumption that the ore has been mined and is available for processing, the first problem to be faced is that of eliminating undesirable components of the natural ore. Most ores contain a certain amount of rock or other earthy materials that do not contain any of the desired metal, and this condition is particularly prevalent among low-grade ores which contain only a small percentage of the desired metal. The method used in concentrating the ore depends upon the character of the naturally occurring material. If the density of the desired component is greater than that of the worthless impurities, the latter often may be removed merely by stirring the finely powdered crude ore with water, thus washing away the lighter fractions and leaving behind a concentrate containing the metal sought. A few minerals are magnetic, and advantage is sometimes taken of this property in effecting a gross separation from nonmagnetic impurities. Most commonly, however, ores are concentrated by the process of *flotation*. This process, which is most frequently employed in the concentration of sulfide ores, involves agitation (by a stream of air) of the finely ground ore with water to which pine oil, "cresylic acids," or other organic materials have been added. The sulfides are carried to the surface by adherence to the resulting froth while sand particles and other heavy materials settle to the bottom. Removal of the material thus brought to the surface followed by removal of adhering water provides a concentrate much richer in the desired metal than the original crude ore. For example, crude low-grade copper ores containing as little as 0.6 per cent Cu are subjected to concentration by flotation and the resulting concentrate (after one flotation) contains as much as 20 per cent Cu. As the richer ore deposits become exhausted, it will become increasingly necessary to resort to the concentration of low-grade ores by flotation or by other suitable procedures.

Roasting. The process of roasting consists in heating the finely powdered ore (either a concentrate or the crude high-grade ore) in the presence of air. This treatment may serve one of three purposes depending upon the nature of the ore: (*a*) Sulfides are converted to the oxide of the metal and sulfur dioxide by reaction with atmospheric oxygen,

$$2MS + 3O_2 \rightarrow 2MO + 2SO_2$$

(*b*) Carbonates are converted to oxides with liberation of carbon dioxide,

$$MCO_3 \rightarrow MO + \overline{CO_2}$$

(*c*) Water, including that held in chemical combination, is removed when the ore is heated.

Smelting. After an ore has been subjected to an appropriate treatment as outlined above or, as is sometimes possible, without any pretreatment, the ore is subjected to a process known as *smelting*. It is in this procedure that the metal is actually obtained in the elemental condition. Although the details differ considerably among the many metallurgical processes in everyday use, the over-all characteristics usually conform to one of the following general methods:

1. *Electrolytic Reduction.* Although perhaps not properly classified as a smelting process, the production of metals by electrolysis may be included at this juncture. In connection with earlier discussions of industrial electrochemical processes (Chap. XXI) examples have been given of the production of active metals by the electrolysis of either fused salts or aqueous solutions.

2. *Reduction by Carbon.* Naturally occurring oxide ores or those produced by the roasting process are frequently reduced by carbon at elevated temperatures. Depending largely upon the temperature employed, an oxide such as the dioxide of germanium may be reduced with direct formation of the metal and carbon dioxide.

$$GeO_2 + 2C + \text{heat} \rightarrow Ge + 2\overline{CO}$$
$$GeO_2 + 2\overline{CO} + \text{heat} \rightarrow Ge + 2\overline{CO_2}$$

In general, reduction by carbon is not suited to the production of metals of a high degree of purity, since the reduced metal usually contains carbon as an impurity.

3. *Reduction by Active Metals.* As has already been indicated (Sec. 21.1), the active metal aluminum was first produced by the reduction of anhydrous aluminum chloride by the more active metal potassium.

$$AlCl_3 + 3K \rightarrow Al + 3KCl$$

However, the most commonly useful application of reduction by active metals is illustrated by the *Goldschmidt process* which involves the high-temperature reduction of oxides or sulfides by active metals such as aluminum or magnesium. This method is used in the case of ores that are difficult to reduce, *e.g.*, the oxides of manganese and chromium. In the reduction of manganese dioxide an intimate mixture of powdered MnO_2 and powdered Al is placed in a clay crucible which is then

embedded in sand (Fig. 112). Into a depression at the top of the charge is placed an ignition mixture consisting of powdered magnesium and either sodium peroxide, barium peroxide, or potassium chlorate into which extends a piece of magnesium ribbon. When the magnesium ribbon is ignited, the heat thereby generated is sufficient to initiate the

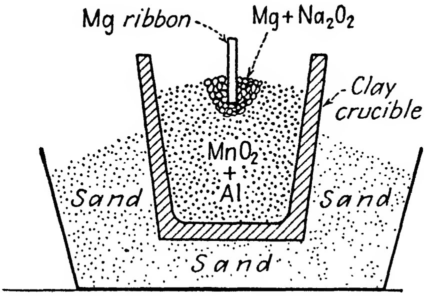


FIG. 112.—Reduction of manganese dioxide by means of aluminum.

combustion of the ignition mixture, and this in turn initiates the strongly exothermal reaction in the charge proper.

$$3MnO_2 + 4Al \rightarrow 3Mn + 2Al_2O_3 + \text{heat}$$

Reactions of this type are so strongly exothermal that the metal is melted and settles to the bottom of the crucible while the aluminum oxide floats on top of the melt. Goldschmidt reduction is particularly

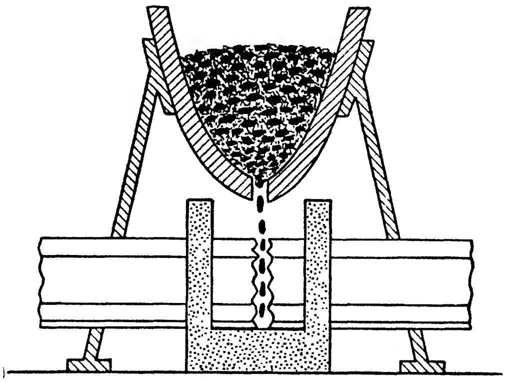


FIG. 113.—The welding of steel rails by the thermite process.

useful when one wishes to prepare metals free from carbon, but it is a relatively expensive method.

The common practice of *thermite* welding is another application of the Goldschmidt process. Iron rails are often welded together by this procedure, as shown in Fig. 113. The ends to be welded together are

surrounded by a packing of sand and clay. Molten iron is produced by the reaction,

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 + \text{heat}$$

and flows through a small opening in the bottom of the crucible and into the space between the ends of the two rails. The temperatures produced by these reactions are often as high as 3500°C.

25.3. Refining Operations

When metals are produced by any of the foregoing procedures or by other methods, the extent to which they must be subjected to purification processes depends upon the applications intended. For many purposes, the crude metals containing appreciable quantities of impurities may be employed; for other applications, extensive refining may be necessary. Since this problem involves so many variables, it seems sufficient merely to indicate the general character of the refining processes most commonly utilized. Purification by electrolysis has already been discussed (Sec. 22.2), and this is unquestionably one of the most important and useful methods. Some metals, notably iron and lead, may be purified by oxidation of the impurities by gaseous oxygen (from air) followed by the removal of the oxidized impurities. Still other metals, such as mercury and zinc, are sufficiently volatile that they may be purified by distillation.

25.4. Physical Properties of Metals

Although the metallic elements exhibit many differences in physical characteristics, the class as a whole is characterized by certain fairly well-defined properties. All metals are similar in that they are (*a*) conductors of electricity, (*b*) conductors of heat, (*c*) opaque to light, and (*d*) reflectors of light. This latter property is usually described by stating that metals exhibit a *metallic luster*, which is silvery in appearance in all cases except copper and gold. Aside from these properties, metals exhibit a wide range of *densities*, from the extremely dense ones such as lead and gold, to the relatively light alkali metals, beryllium, aluminum, etc. All the metals except mercury (a liquid) are solids at ordinary temperatures and exhibit considerable variation in hardness. Thus, although most metals are rather hard substances, some metals, *e.g.*, sodium, lead, etc., are so soft that they may be cut by an ordinary knife. Most of the metals possess the property of *malleability*, *i.e.*, they are capable of being rolled or hammered into thin sheets, and the property of *ductility*, *i.e.*, they are capable of being drawn into wires.

It must be recognized that, in general, the physical properties of any metal are dependent upon (*a*) the crystalline structure of the metal, (*b*) the presence of impurities, and (*c*) the mode of production and the mechanical treatment to which the metal may have been subjected.

25.5. Chemical Properties of Metals

At this point, the student should recall and review numerous important items of information concerning the chemical properties of the metals. Thus, topics that have been considered previously include the relative activity of metals (Secs. 8.2 and 23.3), union of metals with oxygen (Sec. 4.3), reactions between metals and acids, water, and bases (Sec. 8.1), base-forming properties (Sec. 13.5), behavior as reducing agents (Sec. 24.2), etc.

The atoms of the metals in general tend to lose electrons and form positive ions. For this reason, the metals are said to be *electropositive*, and the most electropositive metals are those whose atoms possess a small number of electrons in the outermost orbit (one or two e^-) and hence those which can lose these electrons most readily. With respect to base-forming properties, the strongest bases are formed by the most electropositive metals. Although the metals do exhibit a predominant tendency toward the formation of ionic compounds, metals may also form covalent compounds. This tendency is most prevalent among metals whose atoms contain three or more electrons in the outermost orbit and among the metalloids.

Oxides of the Metals. Although each metal usually combines with oxygen to form an oxide having a composition in conformity with the type formula for the particular periodic group involved (Sec. 13.5), it is generally true that a metal will form oxides of other types as well. For those metallic elements which are capable of existence in various states of oxidation, corresponding oxides may be formed, *e.g.*, Cu_2O and CuO, PbO and PbO_2, MnO, Mn_2O_3, MnO_2, Mn_3O_4, Mn_2O_7, etc. Oxides such as Fe_3O_4 and Mn_3O_4 may be looked upon as *double oxides* in which the valence of the metals becomes more apparent when the formulas are written $FeO \cdot Fe_2O_3$ and $MnO \cdot Mn_2O_3$, respectively. Corresponding to hydrogen peroxide (H_2O_2), which has long been used as an antiseptic, some of the metals also form *peroxides*, of which perhaps the most common are sodium peroxide (Na_2O_2) and barium peroxide (BaO_2). These oxides are characterized by the presence of an oxygen-to-oxygen bond, as shown by the graphic formulas:

$$\mathrm{H{-}O{-}O{-}H}; \qquad \mathrm{Na{-}O{-}O{-}Na}; \qquad \mathrm{Ba}\begin{array}{l} \diagup \mathrm{O} \\ \quad | \\ \diagdown \mathrm{O} \end{array}$$

and by the fact that they react with sulfuric acid with formation of hydrogen peroxide, *i.e.*,

$$\underline{BaO_2} + H_2^+SO_4^= \rightarrow \underline{BaSO_4} + H_2O_2$$

Some oxides having formulas of the type MO_2 are sometimes erroneously called *peroxides*, *e.g.*, PbO_2 and MnO_2. Since these oxides do not possess the properties of true peroxides, it is better simply to designate these as *dioxides*.

Hydrides of the Metals. Combination of metals with hydrogen occurs much less readily than union with oxygen and often leads to products of indefinite and variable composition. Some of the hydrides of the metals are covalent, others are ionic or saltlike in character, while some of the heavier metals appear to absorb, adsorb, or form alloys with hydrogen. In general, the metals exhibit much greater regularity in their behavior toward oxygen than toward hydrogen.

25.6. Alloys

Products obtained by melting two or more metals together and allowing the resulting mixture to cool and solidify are called *alloys*. By far the great majority of the metallic objects encountered in everyday use consists of alloys rather than pure metals. In fact, iron and aluminum are the only metals used extensively in relatively pure form. Some of the more common alloys such as bronze have been known since antiquity and have contributed markedly to the development of modern civilization. Since alloys are of greater practical importance than pure metals, the student should acquire at least some familiarity with the nature, properties, and uses of alloys.

Nature of Alloys. In view of the fact that alloys are *mixtures* (Sec. 1.11), it follows that they may be made up of any desired number of metals and may have any desired composition. For sake of simplicity, the present discussion will be limited largely to the consideration of alloys consisting of *two* metals, *i.e.*, binary alloys. As a result of extensive study, it has been found that when two metals are melted together and the melt is allowed to cool and solidify, the resulting solid will consist of one (or any combination) of the following: (*a*) mixtures of the pure crystals of the two component metals, (*b*) solid solutions, or (*c*) intermetallic compounds. In any event, the character of the solid alloy is dependent upon the specific properties of the metals concerned and upon the proportions in which they were mixed.

The formation of *mixed crystals* results from limited solubility or insolubility of the one solid metal in the other. Lead and tin, and lead and antimony are examples of pairs of metals that form alloys consist-

ing of intimate mixtures of tiny pure crystals of each of the metals. The formation of *solid solutions* results from the fact that the liquid metals may be miscible in all proportions and capable of solidification to solids having compositions essentially the same as those of the melts. Many of the most common and useful alloys consist of homogeneous solid solutions of one metal in the other, *e.g.*, alloys of copper and zinc, gold and silver, nickel and chromium, copper and nickel, etc. *Intermetallic compound* formation occurs in many cases and leads to alloys that are usually too hard and brittle to be of much practical value. However, these very properties may be utilized to advantage in the manufacture of bearing metals, etc., where resistance to abrasion is desired. Typical formulas for intermetallic compounds, Cu_3Sn, $AuMg$, $NaCd_2$, Mn_4Sn, Ca_3Mg_4, Ag_3Bi, etc., show that these compounds often have compositions different from those to be expected on the basis of the normal valences of the metals involved.

The Eutectic. The manner in which the properties of one metal are influenced by the presence of another metal and an understanding of what happens when a solution of one metal in another is allowed to solidify can be understood best by the consideration of a specific example. Pure lead melts at 327°C., and pure antimony melts at 631°C. If a little antimony is dissolved in a large quantity of lead and the resulting solution is cooled slowly, the crystals that appear first consist of pure lead. However, the freezing temperature of the lead that crystallizes from the melt is below 327°C. Similarly, the crystals of pure antimony that separate from a solution of a small quantity of lead in a large quantity of antimony will be found to appear at a temperature below 631°. Thus, each metal lowers the freezing temperature of the other, and it would seem that, for any pair of metals, there will be some particular composition that will exhibit a *minimum* freezing temperature, since the extent of lowering the freezing temperature (analogous to the influence of solutes upon the freezing temperature of water) depends upon the quantity of the second metal added. The relationship between composition and freezing temperature is shown graphically by Fig. 114. *B* represents the melting temperature (freezing temperature) of pure antimony, and the curve *BE* shows the manner in which the melting temperature of antimony is lowered as the percentage of lead is progressively increased. Similarly, *A* represents the melting temperature of pure lead, and the curve *AE* describes the extent to which different percentages of added antimony lower the melting temperature of lead. The point of intersection of the two curves (at *E*) represents the lowest melting mixture of lead and antimony that can be realized. That is, no matter how

many different liquid mixtures of lead and antimony one might prepare, none could be found to have a freezing temperature lower than that represented at *E*. This is known as the *eutectic* of the lead and antimony and corresponds to a composition of approximately 90 per cent of lead and 10 per cent of antimony. The composition of the eutectic is referred to as the *eutectic composition*, and the melting temperature of the eutectic (in this case, 247°) is called the *eutectic temperature.*

If a mixture consisting of 50 per cent of lead and 50 per cent of antimony is melted at 650° (*i.e.*, above the melting temperature of antimony) and the resulting melt is allowed to cool slowly, the first solid will appear when the temperature reaches 500° (*i.e.*, the temperature

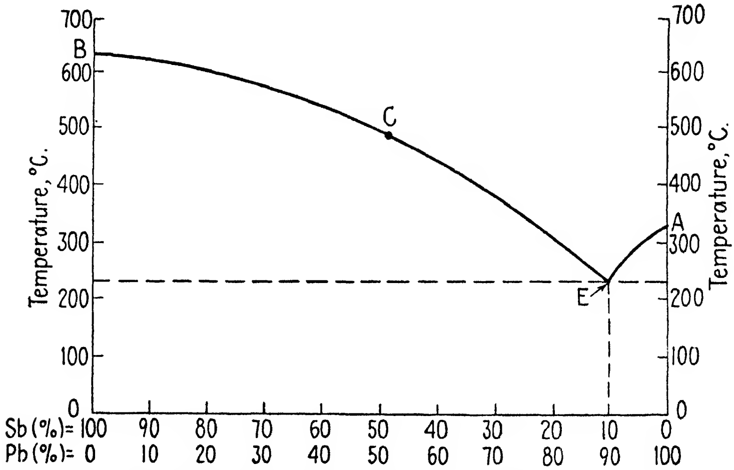


Fig. 114.—The relationship between melting temperature and composition of antimony-lead alloys.

corresponding to point *C* on the curve *BE*). These first crystals will consist of pure antimony and, since antimony is thereby removed from solution, the solution becomes increasingly richer in lead and the temperature of solidification is progressively lowered along the curve *CE* until the eutectic temperature (247°C.) is reached. At this temperature, crystals of both lead and antimony separate from the solution, and the composition of the mixture of the two kinds of crystals is the same as that of the liquid, *viz.*, the eutectic composition. Once the eutectic temperature is reached, crystallization continues to complete solidification of the mixture without any further change in composition.

As is true in most cases, the eutectic of lead and antimony consists of a homogeneous mixture of the crystals of the two metals. This uniform fine texture of the eutectic and its low melting temperature render the eutectic composition particularly useful for many purposes.

Although other compositions are commonly used, it is generally true that the best alloys are those having either exactly or very nearly the composition of the corresponding eutectics.

25.7. Properties and Uses of Alloys

At first glance, it might be assumed that the properties of an alloy formed from two metals would be intermediate between the properties of the component metals. Such is not the case. In general, the properties of an alloy are quite different from those of either of the component metals. It has already been shown (Fig. 114) that the melting temperature of an alloy consisting principally of antimony, but containing some lead, is less than that of pure antimony. On the other hand, the melting temperature of an alloy may be higher (or lower) than that of either component. It is generally true that alloys are harder and poorer conductors of electricity than the pure component metals. When very small amounts of arsenic are alloyed with copper, the electrical conductivity of the copper may be lowered as much as 50 per cent.

It is commonly found that alloys are much more resistant to corrosion (Sec. 27.8) than pure metals. It is largely for this reason that alloys are so widely used in the construction of industrial chemical equipment that must be used in contact with corrosive chemicals. The colors of alloys may not usually be predicted from a knowledge of the colors of the constituent metals. Thus, 5-cent coins are made of copper and nickel and yet are devoid of the color characteristic of copper. Certain alloys of silver and gold are green in color while a certain alloy of beryllium and copper exhibits the characteristic yellow color of gold.

In view of the foregoing facts, it is evident that alloys possessing an almost unlimited variety of properties may be formed. Vast industries concerned almost entirely with the fabrication of alloys have been developed throughout the world. By experiment, alloys "tailored" to fit almost any need are produced and accomplishments recorded thus far represent only a beginning. With hitherto little-known metals becoming more available as a result of improved methods of production, rapid advancement in our knowledge of and uses for alloys is to be anticipated.

The compositions of a few common alloys are listed in Table 32, together with an indication of the outstanding property of each, as well as one or more common uses. Since alloys of iron are to be discussed later (Sec. 27.7), these are not included. A much more extensive tabulation of alloy composition is given in the Appendix.

TABLE 32
COMMON ALLOYS

Name	Percentage composition*	Properties	Uses
Brass	Cu (73–66); Zn (27–34)	Malleable and ductile	Sheets, tubes, wires, etc.
Shot metal	Pb (99); As (1)	Harder than Pb yet readily fusible	Bullets and shot (cast and molded)
Solder	Pb (67); Sn (33)	Low melting	Plumbing
Magnalium	Al (95–70); Mg (5–30)	Light	Scientific instruments
Monel metal	Ni (68); Cu (28); Fe (1.9)	Resistant to corrosion; easily machined and readily polished	Pump cylinders valves, piston rods, etc.
Type metal	Pb (60–56); Sn (10–40); Sb (4.5–30)	Low melting; expands upon solidification	Cast type
Babbitt metal	Sn (89); Sb (7.3); Cu (3.7)	Hard; readily polished	Bearings
German silver	Cu (55); Zn (25) Ni (20)	Hard; readily polished	Substitute for silver
Duralumin	Al (90); Cu (4); Mg (.5); Mn (5.5)	Light; high tensile strength	Airplane and automobile parts, etc.

* It should not be assumed that the composition of commercial alloys will correspond necessarily to the percentages indicated or that other metals may not be present in small amounts. For example, the properties of brass differ with variation in the copper-zinc ratio. Similarly, the properties of a commercial brass are often profoundly changed by the presence of small quantities of other metals. Since alloys are usually fabricated from metals that have not been subjected to elaborate purification processes, the resulting alloys are frequently contaminated with metals present in the ores of the metals primarily concerned.

EXERCISES

1. Distinguish between (*a*) a mineral and an ore, (*b*) the abundance of an element and its availability, (*c*) peroxides and dioxides.

2. Define the following terms: (*a*) native metal, (*b*) metallurgy, (*c*) flotation, (*d*) roasting, (*e*) smelting, (*f*) malleability, (*g*) ductility, (*h*) hydride, (*i*) alloy, (*j*) eutectic temperature, (*k*) eutectic composition, (*l*) eutectic.

3. What types of compounds are most commonly present in the ores of the metals?

4. Should petroleum be classed as a mineral? Why?

5. Into what four steps may metallurgy be divided?

6. What methods are commonly used in the process of smelting? Illustrate each by means of a suitable equation.

7. What is the Goldschmidt process? Illustrate this process by an appropriate equation.

8. Summarize (*a*) the physical properties and (*b*) the chemical properties of the metals.

9. What is implied when an element is said to be electropositive?

10. By what chemical means may one determine whether a given oxide is a true peroxide?

11. With reference to Fig. 114, assume that a mixture consisting of 95 per cent lead and 5 per cent antimony is melted at a temperature of 750°C. Trace the behavior of this mixture as the temperature is lowered slowly to room temperature.

12. In general, what types of behavior may be anticipated when two or more metals are melted together?

13. Indicate clearly the manner and extent of influence exerted by changes in composition (including presence of impurities) upon the properties of alloys.

14. Why are alloys more commonly useful than pure metals?

15. What advantages are involved in the use of alloys having compositions corresponding to their eutectics?

SUGGESTED READING

Journal of Chemical Education

HAYWARD, Extraction of Metals from Ores, **20**, 29 (1943).

FERNELIUS and ROBEY, The Nature of the Metallic State, **12**, 53 (1935).

ROHRMAN, Metals and Alloys in the Chemical Industry, **13**, 53, 106 (1936).

Industrial and Engineering Chemistry

PERCIVAL, DYER, and TAYLOR, Metal Pickling with Ferric Sulfate, **33**, 1529 (1941).

CHAPTER XXVI
HEAVY METALS

Although the various phases of metallurgical operations may be considered in general terms, a true appreciation of the nature of the many problems involved can be had only as the result of the study of specific cases. Consequently, there will be undertaken next a study of the metallurgy of the so-called *heavy metals* and a consideration of related topics. The metallurgy of the light metals has already been discussed (Sec. 22.1), and the metallurgy of iron will be taken up in Chap. XXVII.

26.1. Copper

This metal has been used by man for more than five thousand years and, at present, ranks as one of the most useful heavy metals. Of approximately 2 million tons of copper produced each year, the United States provides ½ million tons.

Occurrence. Small amounts of "native" copper are found in the Lake Superior region and elsewhere in this country. The principal source of this metal, however, consists of compound ores found in Montana, Utah, Arizona, and New Mexico. Of a rather wide variety of copper-bearing minerals, the most important are *chalcopyrite* ($CuFeS_2$), *chalcocite* (Cu_2S), *malachite* [$Cu_2(OH)_2CO_3$], and *bornite* (Cu_3FeS_3). Most other countries produce important quantities of copper, with Chile being potentially one of the chief sources.

Metallurgy. The metallurgy of copper is notable for its simplicity. This fact and the widespread occurrence of native copper are undoubtedly responsible for the early use of this metal. Low-grade copper ores are concentrated by flotation, and the resulting concentrates (or the better grade ores) are roasted in order to accomplish a *partial* conversion of sulfides and a complete conversion of carbonates to oxides. During this treatment arsenic, present as an impurity, is volatilized as arsenious oxide (As_2O_3). The roasted ore, which contains some iron sulfide as an impurity, is then heated with a suitable flux (sand or limestone) in a blast furnace. During this treatment the sulfides of copper and iron are melted and a slag containing the gross impurities separates and is removed. The molten mixture of sulfides

of iron and copper (known as *copper matte*) is transferred to a special type of Bessemer converter (Sec. 27.5), more sand is added, and a blast of air is passed through the resulting mixture. This treatment converts sulfides partly to oxides, and the iron oxide so formed reacts with the sand to form a slag consisting principally of ferrous silicate. The cuprous oxide reacts with unchanged cuprous sulfide to form molten elemental copper.

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + \overline{SO_2}$$

The slag of ferrous silicate floats on top of the molten copper and is poured off, while the molten copper is poured into molds and allowed to cool. This product is known as *blister copper* and ordinarily contains about 2 per cent of impurities among which are several noble metals (Sec. 22.2). Since greater purity is usually required, the blister copper is refined by electrolysis (Sec. 22.2) to provide substantially pure metallic copper. The pure metal has a reddish color, is soft, malleable, ductile, and a good conductor of heat and electricity. It melts at 1083°C., and at room temperature has an absolute density of 8.95.

Uses. The single largest use for pure copper lies in the fabrication of wires and cables for conductors of electricity. Minor and yet important uses include the manufacture of electrical instruments, roofing, coverings for the bottoms of ships, etc. Second only to the production of wires and cables, the manufacture of alloys accounts for the utilization of large quantities of copper, *e.g.*, the various types of brasses, bronzes, coins, etc. (see Appendix). For many years, domestic 5-cent coins have consisted of an alloy of copper (75 per cent) and nickel (25 per cent). However, in order to conserve supplies of both of these important metals, the government in 1942 authorized the issuance of "nickel" coins containing silver (35 per cent), copper (56 per cent), and manganese (9 per cent), *i.e.*, much less copper and no nickel at all. In recent years, alloys of copper and beryllium have been

TABLE 33
IMPORTANT COMPOUNDS OF COPPER

Name	Formula	Uses
Basic copper acetate	$Cu_2(OH)_2(C_2H_3O_2)_2$	Paint pigment
Paris green	$Cu_4(AsO_3)_2(C_2H_3O_2)_2$	Insecticide
Cupric oxide	CuO	Oxidizing agent
Copper sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	Insecticide, medicinal, battery cells, etc.

found to have many useful properties (*e.g.*, hardness, resistance to corrosion, resistance to "fatigue," etc.), and it seems probable that these alloys will become increasingly important among the many known alloys of copper. In addition to the uses for metallic copper, this metal is also used to form many compounds, some of which are of considerable importance commercially. Examples of copper compounds and their uses are given in Table 33.

26.2. Mercury

The chemical inactivity of mercury, its high density, and the fact that this metal is a liquid at ordinary temperatures render it uniquely useful for many purposes in laboratory work in the various sciences. Mercury has been in use since the Middle Ages.

Occurrence. Although small quantities of elemental mercury are found in nature, the mineral *cinnabar* (HgS) constitutes the chief source of this important metal. The richest known deposits of cinnabar are located in Spain and Italy, and these countries have for many years produced the bulk of the world's supply of mercury. Less extensive deposits of cinnabar are found in California, Texas, Oregon, Mexico, Peru, Japan, and China.

Metallurgy. Owing to the instability of mercuric sulfide and mercuric oxide, the metallurgy of mercury is relatively simple. Low-grade ores that have been concentrated by flotation or high-grade ores may be treated in one of two ways. The simplest procedure involves the roasting of the sulfide to produce mercury vapor and sulfur dioxide.

$$HgS + O_2 \rightarrow \overline{Hg} + \overline{SO_2}$$

The mercury vapor is condensed to liquid mercury, and the sulfur dioxide escapes as a gas. Mercuric oxide is not formed since it is unstable at the temperatures employed in the roasting process.

An alternative method involves heating the sulfide in the presence of calcium oxide.

$$2HgS + 2CaO \rightarrow \underline{2CaS} + 2\overline{Hg} + \overline{O_2}$$

In this process, the mercury vapor is condensed and the oxygen permitted to escape.

The first stage in the purification of mercury involves filtration through chamois skin to remove the gross insoluble impurities. If further purification is required, the liquid metallic mercury (containing other *dissolved* metals as impurities) is sprayed into an aqueous solution of mercurous nitrate containing a low concentration of nitric acid.

The impurities react with mercurous nitrate to form water-soluble salts and liberate elemental mercury. The mercury is subsequently separated and dried. If mercury of a high degree of purity is required, the metal may be purified further by distillation under reduced pressure in an apparatus of the type shown in Fig. 115. The pure liquid metal has a silvery color, hence the common name, *quicksilver*. It boils at 356.66°C., freezes at −38.832°C., and has a density of 13.596 at 0°C.

Uses. Mercury is used extensively in thermometers, barometers, and other scientific instruments. Because of its low vapor pressure, its

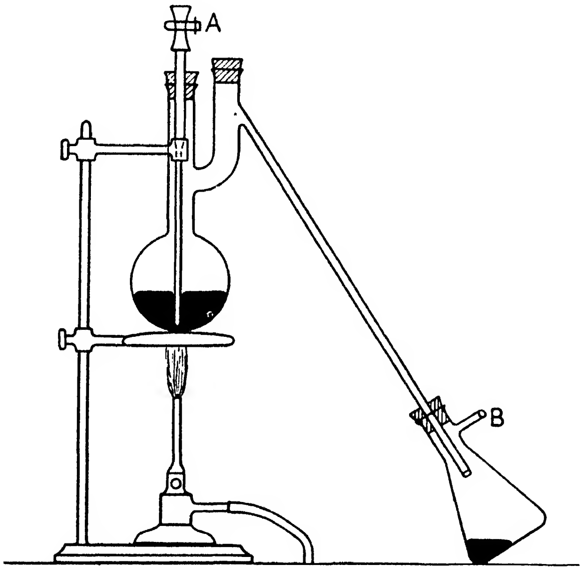


Fig. 115.—Purificatian of mercury by distillation under reduced pressure. The apparatus is partially evacuated by a vacuum pump attached at *B*. By adjustment of clamp *A*, air is permitted to bubble slowly out of the constricted tip of the tube, which extends under the surface of the impure mercury contained in the distillation flask.

high density, and the fact that it is a poor solvent for many common gases, mercury is useful as a confining liquid for work involving the collection and analysis of gases. The metal is also used in mercury-vapor lamps, arc lights, as a substitute for water in the boilers of heat engines, etc. In addition, mercury is used in the form of its alloys (*amalgams*, see below) and in various forms of chemical combination, some of which are listed in Table 34.

Amalgams. Liquid mercury is a fairly good solvent for all metals except iron and platinum. The alloys that are formed by dissolving metals in mercury are called *amalgams*, many of which involve

TABLE 34
IMPORTANT COMPOUNDS OF MERCURY

Common name	Chemical name	Formula	Uses
Calomel	Mercurous chloride	Hg_2Cl_2	Medicinal (liver stimulant)
Bichloride of mercury (corrosive sublimate)	Mercuric chloride	$HgCl_2$	Antiseptic
Ammoniated mercury	Mercuric amidochloride	$Hg(NH_2)Cl$	Medicinal ointment (for skin diseases)
Fulminate of mercury	Mercuric cyanate	$Hg(CNO)_2$	Explosives (percussion caps)
Vermilion	Mercuric sulfide*	HgS	Paint pigment

* A red form of mercuric sulfide which is formed by grinding mercury and sulfur together in the presence of potassium sulfide.

intermetallic compounds of the type MHg_x, where x is quite variable. Aside from their many applications in scientific work, amalgams are used in dentistry and in connection with the metallurgy of silver and gold.

26.3. Silver

Like copper, the metal silver has been known since ancient times and prized as a precious metal. Silver has long been used in the fabrication of jewelry, ornaments, coins, etc.

Occurrence. In addition to native silver, this metal occurs in nature in the form of alloys with gold, mercury, and other metals. In the combined form, practically all the useful ores of silver are sulfides with the single exception of *cerargyrite*, or "horn silver" ($AgCl$). Among the common sulfide ores are *argentite* (Ag_2S), *pargyrite* (Ag_3SbS_3), and *proustite* (Ag_3AsS_3). It is commonly true that sulfides of silver occur in nature along with the sulfides of other heavy metals, and attention has already been called to the fact that important quantities of silver are produced as a by-product of the electrolytic refining of copper (Sec. 22.2).

Metallurgy. As is true in any case, the procedure employed in the metallurgy of silver must be adapted to the particular form in which the metal exists in its ores.

Native silver may be separated by the process of *amalgamation.* The crude ore containing metallic silver is treated with mercury to form an amalgam, which is then separated from the undesired earthy components of the ore. The amalgam is heated in a retort, and the silver remains behind as a residue while the mercury is distilled from the

retort, condensed, and used again. This same process may be used in the extraction of silver from horn silver, but in this case amalgamation is preceded by the reaction

$$2AgCl + Hg \rightarrow 2Ag + Hg_2Cl_2$$

and the silver thus liberated amalgamates with the excess mercury.

Sulfide ores are usually of low silver content and must be concentrated by flotation before further processing is possible. Following concentration, the ores may be treated by any one of several *leaching* processes, two of which will be described briefly. (*a*) The sulfides are converted to sulfates by roasting the ore and the resulting silver sulfate is separated by leaching with water. Metallic silver then is precipitated by addition of copper,

$$Ag_2^+SO_4^= + \underline{Cu} \rightarrow \underline{2Ag} + Cu^{++}SO_4^=$$

separated by filtration, and the copper sulfate that is recovered from the filtrate constitutes an important by-product. (*b*) The sulfide ores are commonly roasted with sodium chloride to form AgCl which is then dissolved by leaching the ore with an aqueous solution of sodium or potassium cyanide. The chloride is dissolved because of the formation of soluble sodium silver cyanide [$NaAg(CN)_2$]. The cyanide solution is treated with finely divided zinc which displaces the silver from the complex cyanide. Sulfide ores of silver and lead are also treated by the Parkes process which will be described in connection with the later discussion of the metallurgy of lead.

Whatever process may be used in the production of crude metallic silver, the product will most likely contain gold, copper, and other metals as impurities. Refining is accomplished by electrolysis from aqueous solutions containing silver nitrate and nitric acid as the electrolyte and by employing crude silver as the anode and pure silver as the cathode (*i.e.*, a method wholly analogous to that used in the case of copper, Sec. 22.2). Silver is also refined by the process of *cupellation* which involves the formation of an alloy with lead, followed by oxidation (in a suitable furnace) of many of the impurities by means of atmospheric oxygen. Following separation of the oxidized impurities, the resulting silver is pure enough for some uses; for other purposes the copper and gold that remain as impurities must be removed by electrolysis, or the silver may be leached with sulfuric acid and the silver displaced from the resulting silver sulfate solution by the addition of copper.

Of all the metals, silver is the best conductor of heat and electricity. Although both malleable and ductile, silver possesses a mechanical

strength which together with its resistance to corrosion makes this metal useful for many purposes.

Uses. Much silver is used in the form of alloys. Alloys of copper and silver are much harder than pure silver and equally or more resistant to corrosion. Sterling silver, silver coins, etc., are alloys of this type. Small amounts of silver are used in the electroplating of a wide variety of objects, in the silvering of mirrors, etc. This metal is of real value in the form of some compounds such as silver nitrate ($AgNO_3$), which is commonly known as *lunar caustic* and which is used in medicine to cauterize wounds and in the manufacture of indelible inks. Silver bromide (AgBr) is an extremely important compound because of its use in photography.

26.4. Photography

No discussion of the uses of silver and its compounds could be complete without reference to the role of these substances in photographic processes. That photography is responsible for the utilization of a considerable fraction of the annual production of silver is shown by the fact that the Eastman Kodak Company alone uses about 300,000 lb. of silver annually.

The use of silver bromide (or less commonly, silver chloride or iodide) depends upon the fact that these salts, when exposed to light, undergo decomposition to an extent that is dependent upon the intensity of the light. The nature of the chemical changes involved in the simplest type of photographic process may be indicated best in terms of the following steps:

1. *Production of the Film or Plate.* A thin layer of gelatin containing a colloidal dispersion of silver bromide is placed upon a film (made of cellulose nitrate or cellulose acetate) or a glass plate. After drying, the film (or plate) is ready for use.

2. *Exposure.* The film or plate is placed in the camera, and the image of the object to be photographed is focused upon the film by means of a suitable lens. Since the object to be photographed has light and dark areas, the light reflected from these areas differs in intensity. Accordingly, the low-intensity reflection from a dark area will result in less activation of the silver bromide on the surface of the film than is produced by the more intense light reflected from light areas. Hence, over the entire surface of the film, varying degrees of activation of silver bromide are realized, and a "latent" or potential image is produced.

3. *Developing.* The latent image on the film is rendered visible by immersing the exposed film in a solution of a reducing agent (the

developer) which is usually an organic compound. Reduction of silver bromide to elemental silver occurs most rapidly in those areas on the film which were exposed to the most intense light. Thus, those parts of the film which are rendered darkest owing to the formation of elemental silver are those corresponding to the lightest parts of the object photographed. If the reducing action of the developer is allowed to proceed indefinitely, all of the silver bromide is reduced and it is therefore necessary to stop the reaction as soon as the image becomes plainly visible.

4. *Fixing.* The film is removed from the reducing solution, unchanged silver bromide is removed by immersing the film in sodium thiosulfate ($Na_2S_2O_3$) (*hypo*) solution, and the film is washed with water and dried. Because the directions as well as the light and dark areas of the object photographed are reversed (for the reason indicated above) the resulting image is called the *negative.*

5. *Printing.* The formation of the finished print or "positive" is accomplished by causing light to pass through the negative and strike the surface of paper which has been coated in much the same manner as is involved in the production of the original film or plate. Because the light must pass through the negative before striking the paper, the light and dark areas on the finished print are the reverse of those on the negative and therefore correspond to those of the object photographed. The process of developing and fixing the print is essentially the same as that involved in the treatment of the negative.

26.5. Lead

Known and used by man for thousands of years, lead is today one of the cheapest and most useful of the heavy metals. The world's annual production of lead amounts to more than 1½ million tons of which nearly 50 per cent is produced in the United States from ore deposits found in Missouri, Oklahoma, Utah, and Idaho.

Occurrence. The single most important ore of lead is the sulfide, *galena* (PbS). Minerals of considerably less commercial value include *anglesite* ($PbSO_4$), *cerussite* ($PbCO_3$), and *wulfenite* ($PbMoO_4$).

Metallurgy. After concentration of sulfide ores of lead (usually by flotation), the concentrate is subjected to an incomplete process of roasting. This treatment converts lead sulfide partly to lead monoxide and lead sulfate

$$4PbS + 7\overline{O}_2 \rightarrow 2PbO + 2PbSO_4 + 2\overline{SO}_2$$

while some of the lead sulfide remains unchanged. At the same time, sulfides of copper, iron, zinc, arsenic, bismuth, etc., which are present

as impurities, are converted to the corresponding oxides. This partly roasted ore is then mixed with limestone (which forms a slag with the silicon dioxide present in the ore), iron ore, and coke. This mixture is heated in a furnace while a blast of air is forced through the mixture and the following changes take place:

$$\begin{gathered}
Fe_2O_3 + C \rightarrow 2FeO + \overline{CO} \\
PbO + C \rightarrow Pb + \overline{CO} \\
PbO + CO \rightarrow Pb + \overline{CO_2} \\
2PbO + PbS \rightarrow 3Pb + \overline{SO_2} \\
PbS + FeO + C \rightarrow Pb + FeS + \overline{CO} \\
PbSO_4 + FeO + 5C \rightarrow Pb + FeS + 5\overline{CO}
\end{gathered}$$

These and undoubtedly several other reactions occur during the smelting of the very complex charge placed in the furnace. As indicated by the above equations, elemental lead may be liberated as a product of five (or more) separate reactions. The lead so produced is drained from the furnace and is then ready for purification. The chief impurities present in the crude product (known as lead *bullion*) are Cu, Ag, Au, As, Sb, and Bi.

Gross impurities are removed by melting the crude lead and forcing a stream of air through the molten metal. Most of the impurities are oxidized, and the resulting oxides float to the surface of the molten lead and are skimmed off. The remaining partly purified lead may be purified further by the *Parkes process* which involves melting of the impure lead and addition of zinc. The zinc dissolves in lead to only a slight extent while the impurities such as copper, silver (Sec. 26.3), and gold are much more soluble in zinc than in lead. After addition of zinc, the molten mixture is stirred and allowed to cool, whereupon the zinc containing the dissolved noble metals rises to the surface and solidifies. After removal of the resulting "crust," the lead is treated successively with fresh portions of zinc until the lead is substantially pure. The zinc crusts containing silver, gold, etc., are heated in a retort; the zinc that distills from the retort is recovered and used again, while the noble metals are reclaimed from the solid residues remaining in the retort. Less commonly, the crude lead bullion is refined by the *Betts process*, which is an electrolytic refining process analogous to that used in the refining of copper. Fluosilicic acid (H_2SiF_6) and lead fluosilicate ($PbSiF_6$) serve as the electrolyte. Large bars of lead bullion serve as anodes, and the cathodes consist of thin sheets of pure lead. During electrolysis, lead is deposited at the cathode, the noble metals collect as a sludge or "mud" in the region of the anode, while the active metals dissolve and remain in the electrolyte. Of the two

methods of refining, the electrolytic method produces the product of greater purity.

Pure lead is a soft, bluish-gray metal which is malleable, ductile, and of very low tensile strength. Lead is a very dense metal (density = 11.34) which melts at 327.50°C. and boils at about 1600°C. The hardness of lead is usually increased markedly even by small quantities of metallic impurities.

Uses. The chief uses of lead are found in (*a*) the construction of storage batteries (Sec. 23.6), (*b*) the manufacture of a wide variety of alloys (see Appendix), (*c*) the coating of iron wires and cables (Sec. 27.9), (*d*) the construction of "lead chamber" sulfuric acid manufacturing plants, and (*e*) the production of many useful compounds, one of the most important being basic lead carbonate which is extensively used as a white paint pigment. Some of the more common and useful compounds of lead are listed in Table 35.

TABLE 35

IMPORTANT COMPOUNDS OF LEAD

Common name	Chemical name	Formula	Uses
Litharge.........	Lead monoxide	PbO	Manufacture of glass, pottery, cements
	Lead dioxide	PbO_2	Manufacture of storage batteries
Minium (red lead)	Plumbous plumate*	Pb_3O_4	Paint pigment
Sugar of lead.....	Lead acetate trihydrate	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	Medicinal
Sublimed white lead	Basic lead sulfate	$Pb_2O(SO_4)$	Paint pigment (white)
White lead.......	Basic lead carbonate	$Pb_2(OH)_2CO_3$	Paint pigment (white)
Chrome yellow...	Lead chromate	$PbCrO_4$	Paint pigment
Chrome red......	Basic lead chromate	Pb_2OCrO_4	Paint pigment
	Lead arsenate	$Pb_3(AsO_4)_2$	Insecticide
	Lead tetraethyl	$Pb(C_2H_5)_4$	Antiknock in motor fuels

* So-called because this compound is actually the lead salt of orthoplumbic acid (H_4PbO_4) *i.e.*, $Pb_2(PbO_4)$.

26.6. Tin

The mineral *cassiterite* (SnO_2) is the only important ore of tin. About 165,000 tons of tin are produced annually, most of which comes from cassiterite deposits found in British Malaya, Netherlands East Indies, Bolivia, Belgian Congo, Nigeria, and Siam. Although the United States consumes nearly one-half of the tin produced, no significant amounts are produced from the very scarce and low-grade domestic ores. A tin smelter located on the Texas Gulf coast (Fig. 116)

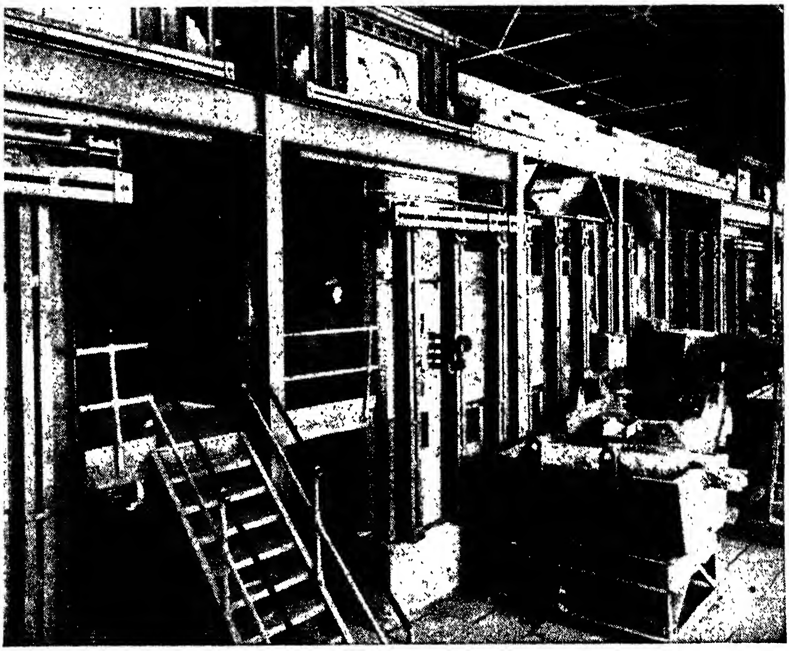


FIG. 116 –View of a portion of a tin smelting plant located at Texas City, Texas. (*Courtesy of Alex. L. ter Braake, Tin Processing Corporation.*)

produces tin from cassiterite concentrates imported from Bolivia, the Netherlands East Indies, and Belgian Congo.

Metallurgy. Concentrated cassiterite ores are roasted largely for the purpose of removing arsenic and sulfur (as As_2O_3 and SO_2) and converting metallic impurities into their oxides. These oxides are then removed by leaching with dilute sulfuric acid in which the SnO_2 is insoluble. The prepared concentrate is thereafter reduced by carbon in a reverberatory furnace.

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

The molten tin is removed, cast into blocks ("block tin"), and sub-

sequently purified by a number of refining processes, the most effective of which is an electrolytic process similar to that used in the refining of lead.

Uses. The most important uses for tin are concerned with the manufacture of tin plate (sheet iron coated with tin, Sec. 27.9), a variety of alloys, tin foil, and pipes which, being very resistant to corrosion, are used to carry water and other liquids

26.7. Zinc

The history of the metal zinc is interesting in that it was long used in the form of alloys before it came to be recognized as an element in 1746. For hundreds of years prior to this date, however, alloys of copper and zinc (brasses) were produced by the smelting of ores containing compounds of these two metals.

Occurrence. Zinc occurs in a rather wide variety of combinations in nature. The chief ores of this metal are *sphalerite* or "zinc blende" (ZnS) and *franklinite* which is a rather complex mixture consisting largely of the oxides of zinc and iron together with variable quantities of oxides of manganese. Other zinc-bearing minerals include *smithsonite* or "zinc spar" ($ZnCO_3$), *zincite* (ZnO), *willemite* (Zn_2SiO_4), and *calamine* ($Zn_2H_2SiO_5$ or $Zn_2SiO_4 \cdot H_2O$). In the United States, the most important zinc-producing areas are the franklinite deposits in New Jersey and the rich deposits of sphalerite in a region comprising parts of the states of Oklahoma, Kansas, and Missouri.

Metallurgy. The most modern method for the production of zinc is the electrolytic process which has already been described (Sec. 22.1). An older metallurgical process, which is still used extensively, involves a rather extended treatment of high-grade ore or concentrates obtained by a flotation process. In either case, the finely divided ore is roasted to convert sulfides and carbonates to oxides which are then reduced by means of carbon at temperatures within the range 1200° to 1300°C. Since zinc boils at 907°C., the liberated metal distills from the earthenware retort and may be condensed in suitable receivers. If the temperature of the condenser is kept below the melting temperature of zinc (*i.e.*, 419.3°C.), the metal is obtained in the form of zinc dust which, in addition to metallic impurities, contains approximately 5 per cent of zinc oxide. If, however, the zinc vapors are condensed at a temperature above 419.3°, the metal is obtained in the liquid form and is subsequently poured into molds and cooled. The crude metal obtained in this manner is known commercially as zinc *spelter*.

The principal impurities in zinc spelter are cadmium, iron, lead,

arsenic, and copper. In addition to purification by electrolysis (Sec. 22.1), zinc spelter may be refined by redistillation or by suitable chemical methods chosen in relation to the desired degree of purity.

Metallic zinc is characterized by a brilliant white luster which tarnishes readily to produce the familiar dull gray appearance. Between 100° and 150°C., the metal is both malleable and ductile. Pure zinc melts at 419.3°C. and boils at 907°C. The density of cast zinc is 6.94 while that of rolled zinc is 7.14.

Uses. The major uses of metallic zinc are in the manufacture of alloys (see Appendix) and in the use of zinc as a protective coating on other metallic products, notably iron and steel (Sec. 27.9). Lesser quantities are employed in the manufacture of dry cell batteries (Sec. 23.8), sinks, gutters, cornices, weather strips, etc. The use of zinc in connection with the metallurgy of lead has been described previously (Sec. 26.5). In chemical laboratory work, zinc is one of the most widely used reducing agents.

Zinc oxide (ZnO), which is produced by burning zinc vapor in atmospheric oxygen, is by far the most important compound of zinc. Under the name of *zinc white*, the oxide is used as a paint pigment. It is also used as a base in the manufacture of enamels, glass, and as a "filler" in the fabrication of automobile tires and other kinds of rubber goods. Zinc sulfide (ZnS) is also an important white paint pigment which is used either as such or in the form of *lithopone*, which is a mixture of zinc sulfide and barium sulfate. This widely used pigment is prepared by the metathetical reaction between zinc sulfate and barium sulfide,

$$Zn^{++}SO_4^{=} + Ba^{++}S^{=} \rightarrow \underline{ZnS} + \underline{BaSO_4}$$

a reaction in which both of the products are insoluble. Another useful compound of zinc is the chloride, $ZnCl_2$, which is used as a wood preservative, as a soldering fluid to remove oxides from metallic surfaces, and in the production of parchment paper.

26.8. Other Heavy Metals

The preceding examples and the treatment of the metallurgy of iron (Chap. XXVII) are typical of the processes involved in the production of metals of relatively high density. Since the time available for detailed study of individual metals is necessarily limited in any beginning course in chemistry, the remaining heavy metals that are used industrially will not be considered in detail. However, in order that the student may gain some idea as to the mode of occurrence and the metallurgy and uses of these metals, a limited selection of information of this character is provided in Table 36.

TABLE 36
SOME IMPORTANT HEAVY METALS

Metal	Mode of occurrence in nature	Nature of metallurgical process	Uses of the metal
Cadmium..	Associated with zinc minerals*	By-product of the refining of zinc spelter	In manufacture of alloys and as a protective coating for other metals
Bismuth...	Native, and as bismite ($Bi_2O_3 \cdot H_2O$)	Melting of native metal followed by separation of earthy impurities	In production of low-melting alloys
Chromium.	Chromite [$Fe(CrO_2)_2$]	Reduction of oxide by carbon†	In electroplating and in manufacturing of corrosion-resistant alloy steels
Manganese	Pyrolusite (MnO_2)	Reduction of oxide by carbon or by aluminum‡	Manufacturing of alloys with iron and other metals
Nickel.....	*Pyrrhotite*, a mixture of sulfides of Ni, Fe, and Cu	Reduction of oxide by carbon	Manufacturing of alloys, in electroplating, and as a catalyst
Platinum..	Native, and as sperrylite ($PtAs_2$)	Native Pt is dissolved in *aqua regia*, precipitated as $(NH_4)_2PtCl_6$ which is then decomposed by heat → Pt	As catalyst; as adsorbent for gases; in manufacturing of jewelry, electrical instruments, electrodes, crucibles, etc.

* The mineral, *greenockite* (CdS) occurs in nature mixed with sphalerite.

† Unless the iron is first removed, reduction of *chromite* by carbon produces the iron-chromium alloy, *ferrochrome*, which is used in the manufacture of chromium steels.

‡ *I.e.*, the Goldschmidt process (Sec. 25.2).

EXERCISES

1. List the mineral names, chemical names, and formulas of two important ores of each of the following metals: (*a*) copper, (*b*) silver, (*c*) lead, (*d*) zinc.

2. Identify the following terms: (*a*) blister copper, (*b*) amalgamation, (*c*) leaching, (*d*) cupellation, (*e*) zinc dust, (*f*) zinc spelter, (*g*) lunar caustic.

3. For what purpose is each of the following used: (*a*) the Betts process? (*b*) the Parkes process?

4. Listed below are the common names of several important paint pigments. In each case, write the corresponding chemical formula (or formulas): (*a*) lithopone, (*b*) chrome yellow, (*c*) zinc white, (*d*) red lead, (*e*) vermilion, (*f*) white lead.

5. In the case of each of the following compounds, write the chemical name, the common name, and one important use: (*a*) $ZnCl_2$, (*b*) Hg_2Cl_2, (*c*) $AgNO_3$, (*d*) $Hg(CNO)_2$, (*e*) $Cu_4(AsO_3)_2(C_2H_3O_2)_2$; (*f*) $HgCl_2$, (*g*) ZnO, (*h*) $Pb(C_2H_3O_2)_2 \cdot 3H_2O$.

6. Outline briefly the major steps involved in the metallurgy of (*a*) silver, (*b*) copper, (*c*) lead.

7. In what physical property does mercury differ from all other metals?

8. What is the function of a slag as used in metallurgical processes?

9. Make a tabulation of the metals discussed in this chapter and the commercial uses for these metals.

10. In photography, what is the meaning of the following terms: (*a*) negative, (*b*) hypo, (*c*) developer, (*d*) latent image, (*e*) positive?

11. Trace the consecutive steps involved in a simple photographic process and indicate the nature of the chemical changes involved in each.

12. Write equations representing: (*a*) the formation of elemental copper from a mixture of cuprous oxide and cuprous sulfide, (*b*) two methods for the liberation of mercury from *cinnabar*, (*c*) the roasting of *galena*, (*d*) the reduction of *cassiterite* by carbon.

13. How many tons of tin may be obtained from 63 tons of an ore consisting of 88 per cent *cassiterite* if the metallurgical process (reduction by carbon) has an over-all efficiency of 94 per cent?

SUGGESTED READING

Journal of Chemical Education

HOWARD, The Story of Copper, **6**, 413 (1929).

SULLIVAN, Leaching Copper from Its Ores, **8**, 829 (1931).

SHEPPARD, The Chemistry of Photography, **4**, 298, 465, 749 (1927).

CARROLL, The Preparation of Photographic Emulsions, **8**, 2341 (1931).

MEES, The Process of Color Photography, **5**, 1385, 1577 (1928); **6**, 44, 286 (1929).

HANLEY, The Story of Zinc, **10**, 600, 682 (1933); **11**, 33, 111 (1934).

VACHER, Oxygen, Nitrogen, and Hydrogen as Constituents of Metals, **9**, 47 (1932).

Industrial and Engineering Chemistry

CARTER, Precious Metals as Materials of Construction, **27**, 751 (1935).

Metals and Alloys

DELMONTE, Beryllium and Its Alloys, **7**, 175, 211, 239 (1936).

CHAPTER XXVII

IRON AND STEEL

Of all the many and varied aspects of the chemistry of metals, the industrial importance of iron and the various products derived therefrom is traditionally singled out for special emphasis. It is certainly true that the many rich deposits of high-grade iron ores, the relative ease and low cost with which the metal may be extracted, and its many useful properties, have made iron the cornerstone of industrial development in this and other countries. Although modern trends in the metallurgical industries indicate rather clearly that certain of the light metals (Sec. 22.1) may eventually come to rival the dominant position of iron, many years will elapse before it is relegated to a position of secondary importance.

27.1. Ores of Iron

Iron occurs in nature in a wide variety of conditions of chemical combination. Of these, oxides, sulfides, and carbonates are the compounds used as commercial sources of iron. *Hematite* (Fe_2O_3) is by far the most important. Other iron ores used to a lesser extent include *limonite* [$(Fe_2O_3)_2 \cdot 3H_2O$], *magnetite* ("magnetic oxide of iron") (Fe_3O_4), *siderite* ($FeCO_3$), and *pyrite* (FeS_2).

Most of the countries having any marked degree of industrial development have readily available deposits of iron ores. In the United States, the Lake Superior region (Minnesota, Michigan, and Wisconsin) furnishes about 85 per cent of the domestic production while the remainder is obtained from ores located in Alabama, New York, Colorado, California, Virginia, Tennessee, Ohio, and Texas. In the Lake Superior region, the famous Mesabi iron range employs the open-pit method of mining and is one of the world's most important iron-producing areas. From this and other near-by ranges, *hematite* ore is produced at a rate of 90 million tons per year. So rich are these deposits that only the high-grade ores have been utilized. However, it has been estimated that these "pockets" of almost pure *hematite* will be exhausted by 1950 and it will then become necessary to resort to the use of lower quality ore either from the same area or from deposits located elsewhere. This fact in itself may have an important bearing

upon the future of the iron and steel industry as its competitive position is rendered increasingly more difficult as a result of increased costs brought about by the necessity of processing the poorer ores.

27.2. Metallurgy of Iron

From the standpoint of the chemical changes involved, the production of iron from an oxide ore (or from a carbonate or sulfide ore after roasting) may be represented in terms of a few simple reactions. The raw materials required are the ore, limestone, and coal or coke. The carbon in coal or coke is first changed to carbon dioxide, which in turn is passed over layers of hot coke to convert the dioxide to carbon monoxide.

$$\overline{CO}_2 + C \rightarrow 2\overline{CO}$$

The resulting monoxide serves to reduce the iron oxide to elemental iron through a series of steps which occur at the indicated approximate temperatures:

$$3Fe_2O_3 + \overline{CO} \xrightarrow{450°\text{C.}} 2Fe_3O_4 + \overline{CO}_2$$

$$Fe_3O_4 + \overline{CO} \xrightarrow{600°\text{C.}} 3FeO + \overline{CO}_2$$

$$FeO + \overline{CO} \xrightarrow{800°\text{C.}} Fe + \overline{CO}_2$$

The iron is liberated in a spongy condition and absorbs from 4 to 4½ per cent of carbon before it melts at about 1150°C. During the progressive increase in temperature, the limestone decomposes to form quicklime,

$$CaCO_3 \xrightarrow{800\text{–}900°\text{C.}} CaO + \overline{CO}_2$$

which combines with silicon dioxide (sand) always present in the ore to form *liquid* calcium silicate.

$$CaO + SiO_2 \xrightarrow{1000\text{–}1200°\text{C.}} CaSiO_3$$

This molten calcium silicate and the other more readily fusible silicates that are always present in the crude iron ores form a slag which floats on the surface of the molten iron. The slag is removed, allowed to solidify, and used in the manufacture of cement or as a road-building material after being mixed with asphalt or road tar.

27.3. Operation of the Blast Furnace

The chemical reactions indicated above occur in a device known as a blast furnace (Fig. 117). The blast furnace is a tall slightly conical

tower about 90 ft. in height and from 20 to 25 ft. in diameter at the widest region. The furnace is built of heavy steel plate and lined with firebrick. Hollow bronze brick, through which water is circulated, are inserted in the walls to keep the brick from melting. A double-cone charging device is located at the top, while a pit for the temporary collection of iron and slag is provided at the bottom. At the sides and near the bottom are provided water-jacketed openings

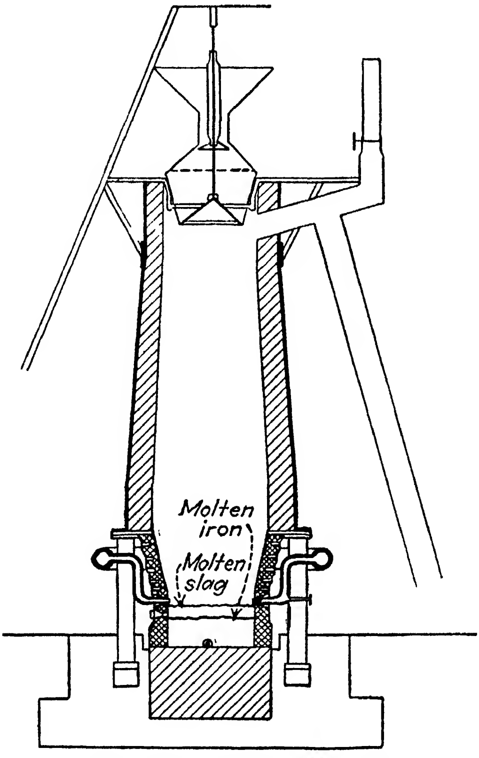


FIG. 117.—The blast furnace.

(tuyères) through which a blast of air heated to 425° to 600°C. is sent into the furnace. The charge which is introduced at the top of the furnace consists of definite quantities of iron ore, coke, and limestone. The coke burns to form carbon dioxide and carbon monoxide near the openings of the tuyères, and these gases pass upward to heat the charge.

When the rising gases have heated the charge to about 450°C., the carbon monoxide begins to change the iron ore into Fe_3O_4. At about 600°C., the Fe_3O_4 is converted to FeO and, as the charge sinks and gets hotter (750° to 800°C.), the ferrous oxide is reduced to spongy elemental iron which absorbs carbon from the glowing coke until a tem-

perature of about 900° is reached, after which no more carbon is absorbed.

Within the temperature range of 800° to 900°C., the limestone decomposes to form CO_2 and CaO, and the latter reacts with sand (present in the crude ore) to form the readily fusible calcium silicate ($CaSiO_3$). This, together with other melted silicates (which are present in all crude iron ores), constitutes the slag, the formation of which is complete at 1100° to 1200°C. At these temperatures, both the slag and the iron are in the molten condition, and the slag forms a liquid layer which floats on the surface of the molten iron.

In a 24-hr. period of operation, slag is removed at the "cinder notch" about fifteen times while iron is removed at the "iron notch" every 6 hr. The molten iron is allowed to solidify in sand molds or clay-lined molds or is used immediately in the production of steel without ever being allowed to solidify. The larger portion of the iron produced in the United States never cools from the time it is first heated in the blast furnace until it is ready to be sent out from the steel mills in the form of rails, structural steel, tin plate, etc.

The gas escaping from the blast furnace through the large "downcomer" pipe contains from 22 to 25 per cent of carbon monoxide and has a heating value of about 90 to 95 B.t.u. per cu. ft.[1] This gas is led through a dust catcher (the "cyclone") and is then used as a fuel. About one-third of this gas is burned in a series of four hot-blast stoves for preheating the dry air that goes into the blast furnace at the tuyères; the remaining two-thirds is used in gas engines to generate power for the mills surrounding the blast furnace. The operation of a single blast furnace for a 24-hr. period requires from 4000 to 5000 tons of air, 500 to 600 tons of limestone, 1500 to 1600 tons of iron ore, and produces about 1000 tons of iron.

27.4. Varieties of Iron; Their Properties and Uses

Molten iron from the blast furnace may be drained into sand molds or clay-lined molds and allowed to cool. The resulting ingots weigh about 150 lb. each and are known as *pig iron* or *cast iron*. This relatively impure product contains some slag in addition to the following impurities: carbon (2 to 4.5 per cent), silicon (1 to 2 per cent), sulfur (0.1 to 0.3 per cent), phosphorus (0.1 to 2.0 per cent), and manganese (0.5 to 1 per cent). This product, because of the presence of the indicated impurities, has a melting temperature lower than that of

[1] B.t.u. is the abbreviation for the British thermal unit which is the quantity of heat required to raise the temperature of 1 lb. of water (at its maximum density) 1°F. One B.t.u. is equivalent to 252 cal.

pure iron, is hard, brittle, and exhibits low tensile strength and ductility.

Cast Iron. When scrap iron is added to molten pig iron and the resulting liquid is allowed to cool in suitable molds, cast iron is formed. The rust (Fe_2O_3) on the surface of the scrap iron oxidizes partly (at the temperature of the molten mixture) some of the impurities in the crude pig iron, *e.g.*,

$$3S + 2Fe_2O_3 \rightarrow 4Fe + 3SO_2\uparrow$$

It should be recalled also that, during its formation in the blast furnace, iron absorbs carbon. These two elements combine to form iron carbide (Fe_3C), which is also known as *cementite.* In the production of cast iron, the character of the product is dependent upon the extent to which the iron carbide is decomposed. If the mold is chilled so that the iron cools rapidly, most of the iron carbide remains as such and *white cast iron* is produced. This product is hard, brittle, and cannot be machined. If, on the other hand, the molten iron is cooled slowly, *gray cast iron* is obtained and in this process part of the Fe_3C decomposes to form iron and carbon. This variety is much softer and tougher than white cast iron and can be machined and drilled successfully. If molten pig iron to which scrap iron has been added is maintained at 400° to 600°C. for several days until practically all of the cementite has decomposed, the resulting product has a high content of uncombined carbon and is known as *malleable cast iron.* This material expands upon cooling and is very useful in the manufacture of stoves, machinery bedplates, radiators, and other articles not subjected to shock during use. Thus, it is evident that the essential difference between white, gray, and malleable cast iron depends upon the extent to which carbon is present in the uncombined form, and this factor also governs the properties of the three varieties of cast iron.

Wrought Iron. In 1784, an Englishman, Henry Cort, devised a method for the conversion of pig iron into a much more useful product known as *wrought iron.* This conversion is accomplished by removal of most of the impurities from pig iron by oxidation in a "puddling" or reverberatory furnace. The furnace is lined with magnesium oxide and is charged with about ¼ ton of pig iron together with some nearly pure hematite ore which serves as a source of oxygen. Upon heating, carbon is oxidized to carbon dioxide which escapes as a gas while silicon, phosphorus, and manganese are oxidized to the corresponding oxides. Some of the manganese reacts with sulfur to form manganous sulfide. The acidic oxides of silicon and phosphorus combine with the basic lining of the furnace to form magnesium silicates and phosphates,

which together with the oxides and sulfides of manganese constitute a molten slag. As the impurities are removed, the melting temperature of the iron is raised until it finally becomes partly solidified; whereupon it is rolled into large balls or *blooms* and taken out of the furnace to be rolled into sheets. This rolling process squeezes out most of the adhering slag, also lengthens out the crystals of the iron, and incorporates any remaining slag rather uniformly. The resulting wrought iron is the purest form of commercial iron but still contains usually about 1 per cent of slag (the presence of which is desirable since it improves the tensile strength) and about one-tenth of 1 per cent of carbon.

This form of iron has great tensile strength, can be forged and welded, is ductile and malleable, and has a relatively high melting temperature. Wrought iron has a somewhat fibrous structure, owing to small pockets of slag, and is therefore rather difficult to machine. Some wrought iron is used in the manufacture of high-quality tool steel, but the chief uses are in the manufacture of wire, chains, rails, anchors, bolts, nails, rivets, grate bars, pipes, etc.

27.5. Production of Steel

Steel is the name given to iron which contains from 0.04 to 1.7 per cent of carbon, small percentages of manganese, only very small amounts of impurities such as sulfur and phosphorus, and which is capable of being hardened by quenching (*i.e.*, rapid cooling by immersion in water, oil, or other suitable liquid). The carbon content of steel must be kept below 2 per cent in order to prevent excessive brittleness. Steel is produced either from pig iron or from wrought iron by several processes, each of which will be considered briefly.

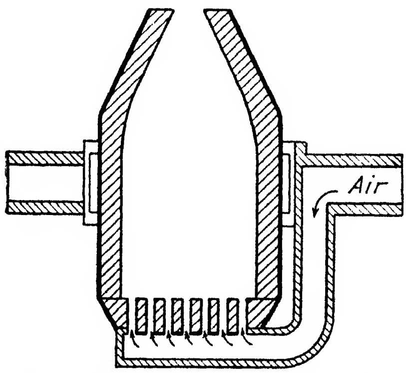


FIG. 118.—The Bessemer converter.

Bessemer Process. The essential features of this process were introduced by the American, William Kelley, in 1852. However, an improved form of this process was discovered and patented by the Englishman, Sir Henry Bessemer, in 1855; hence the name *Bessemer process.* The process employs a pear-shaped vessel (Fig. 118) from 12 to 20 ft. in height, 10 to 16 ft. in diameter, and mounted on trunnions in order that it may be turned on its short axis for loading and

unloading the charge. Th's vessel is known as a *converter* and is lined to a thickness of about 2 ft. with an *acidic* refractory material consisting largely of silica (SiO_2) and silicates bound together with fire clay. One of the trunnions is hollow and leads to a series of tuyères in the bottom of the converter through which a blast of air is admitted.

The converter is charged with approximately 20 tons of molten pig iron, *preferably having a low phosphorus content*, and with the converter in a vertical position, a blast of air is blown through the charge. Silicon, manganese, and carbon burn away (in the order named) so violently that the temperature of the charge is raised considerably. Phosphorus is burned to form the oxide (P_2O_5), but this does not enter the slag and hence is not removed. In about 10 or 15 min. the "blow" is completed and the charge remaining in the converter consists of nearly pure iron. Before the melt is poured from the converter, the required amounts of manganese, carbon, and silicon are added in the form of *spiegeleisen* which is an iron-manganese alloy of high carbon content. The manganese removes sulfur and combined oxygen; silicon removes trapped air bubbles; and at the same time the carbon content is brought up to the desired percentage. The resulting molten steel is transferred to molds and cast in the form of ingots which may weigh as much as 4 tons.

The Bessemer process is relatively less expensive but does not produce a product of high quality. It is not possible to exercise control over the composition of the product because the conversion occurs so quickly. Furthermore, this process does not effect the removal of phosphorus. The phosphorus pentoxide that is formed during the blow is reduced to phosphorus upon addition of carbon and hence remains as an impurity in the final product. Provision for the removal of phosphorus may be made by the use of the so-called *basic* Bessemer process which employs a converter lined with magnesia (MgO), but this practice entails other disadvantages. In the United States, the *acid* Bessemer process is used exclusively and accounts for about 15 per cent of the steel produced in this country. Steel so produced is used largely as structural steel, as reinforcement for concrete, and in the tin-plate industries.

Despite its disadvantages and limitations, the invention of the Bessemer process opened a new era of industrial progress. Through its use, cheap steel became available and was largely responsible for the rapid expansion of railroad building during the latter part of the nineteenth century.

Open-hearth Process. Only a few years after the invention of the Bessemer process, the use of open-hearth gas-fired furnaces was

adapted to the production of steel. The open-hearth furnace (Fig. 119) is built of brick and steel and contains a shallow saucerlike basin (hearth) capable of carrying a charge of 70 to 100 tons of pig iron. This hearth may be lined either with an acidic (SiO_2) or basic (MgO) lining but, since American practice is limited to the basic process, the other possibility will not be discussed further. In the basic process, 70 to 100 tons of pig iron together with rusty scrap iron or steel, limestone, and oxides of iron constitute the charge. Air and gas are introduced through separate flues and are passed through a heated checker-brick structure before coming into contact with the charge.

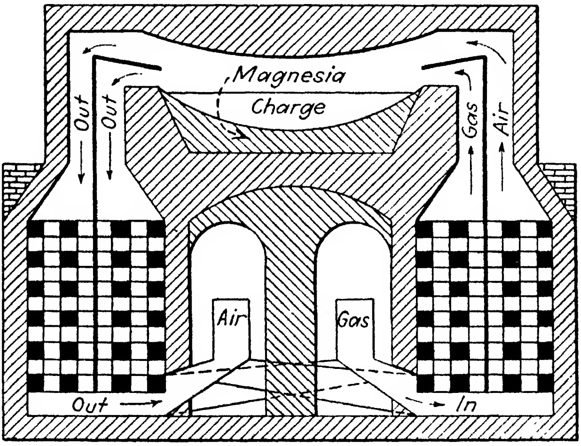


FIG. 119.—The open-hearth furnace.

Combustion of the gases heats the charge, and the hot gases pass out through and heat the checker-bricks on the opposite side of the furnace. Then the current of gases is reversed so that the incoming gas flow will pass through the newly heated bricks. Thus, frequent reversal of direction of flow of gases maintains a high temperature and conserves fuel.

In the molten charge, silicon, *phosphorus*, sulfur, manganese, and carbon are converted to the corresponding oxides by reaction with iron oxide (Fe_2O_3). Oxides of carbon and sulfur pass off as gases while the oxides of phosphorus and silicon combine with calcium oxide (formed by the decomposition of the limestone) to form phosphates and silicates.

$$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$

At the same time manganous oxide reacts with silicon dioxide to form manganous silicate.

$$MnO + SiO_2 \rightarrow MnSiO_3$$

These phosphates and silicates form a slag. Thus *all* the impurities are removed from the molten iron in a period of from 7 to 8 hr. Near the end of the period of treatment, samples of the molten iron are removed, solidified, and sent to the chemical laboratory for accurate and rapid quantitative analysis. On the basis of information supplied by the laboratory, it becomes possible to calculate accurately the quantity of *spiegeleisen* which must be added in order to produce a steel of the desired composition. Thereafter, the molten steel is transferred to molds where the steel is cast into ingots.

In comparison with the Bessemer process, the open-hearth process has certain important advantages. It provides accurate control of temperature owing to the use of an outside source of heat. The composition of the final product can be predetermined by analysis and thereby controlled. Complete removal of phosphorus is accomplished, and this permits use of low-grade iron ores which are usually of relatively high phosphorus content. None of these advantages is possessed by the Bessemer process.

More than three-fourths of the steel produced in this country is produced by the open-hearth process. The uses are innumerable and include practically every commercial application except those in which special alloys must be employed.

Crucible Process. This process utilizes either wrought iron or open-hearth steel. The iron (or steel) is melted in graphite-clay crucibles in gas or electric furnaces, and pure carbon introduced to bring the carbon content up to 0.8 to 1.5 per cent. The steel thus produced is a uniform product of high quality and relatively high cost. It is used in making knives, razor blades, and tools requiring definite carbon content.

Cementation Process. This process, now little used, consists in heating wrought iron or low-carbon steel in powdered charcoal or leather dust for 6 to 11 days in a closed box-like furnace at 650° to 700°C. At these temperatures, carbon diffuses slowly into the *surface* of the steel thus producing a thin coat of high-carbon steel over a core of low-carbon steel. This procedure is essentially one of casehardening, and steel produced in this manner is used largely in the manufacture of tools.

Electric-furnace Process. One of the highest grades of steel now produced is made through the use of electric furnaces in which steel from the Bessemer or open-hearth process is subjected to further refining. The steel produced in this relatively new process is characterized by its high density and the absence of occluded gases. The

chief advantage of this process is its provision for more precise control of temperature.

27.6. Influence of Impurities upon the Properties of Iron

By inference from previous discussions of other commercial processes, one may gain the impression that the objective of all industrial chemical operations is the production of products of high purity. This is not so in the case of iron. The properties of pure iron are not such as to render this metal particularly useful, and the problem therefore becomes one of producing impure iron containing just enough of the right impurities to impart to the iron a desirable set of mechanical properties. The influence of these impurities can be discussed only in general terms since the properties imparted by any one impurity may be modified by the presence of one or more other impurities.

Carbon, added to iron, may exist in the iron in the combined form, *i.e.*, Fe_3C, or as elemental graphitic (Sec. 28.3) or flake carbon. Combined carbon increases hardness and mechanical strength in cast iron and steel; graphitic carbon decreases both strength and hardness.

Silicon acts as a softener in cast iron, increases fluidity, lessens shrinkage, and decreases the strength. Cast iron containing from 15 to 20 per cent silicon is very resistant to the action of acids. Since steel and wrought iron contain no more than traces of silicon, it has no appreciable influence so far as these products are concerned.

Sulfur tends to change graphitic carbon into combined carbon (Fe_3C), thus indirectly increasing the hardness, brittleness, and shrinkage of cast iron (and to a lesser extent, of steel). Presence of more than 0.1 per cent of sulfur renders iron very weak and dangerously brittle *when hot.*

Phosphorus increases the fluidity and softness of cast iron while decreasing the shrinkage and strength. In steel, phosphorus decreases ductility and increases slightly the hardness and tensile strength of low-carbon steels. In general, however, a high phosphorus content causes steel to fracture easily when subjected to strain or deformation *when cold.*

Manganese is known as a *cleanser* of iron, inasmuch as it combines with any unchanged iron oxides or sulfides, thus removing oxygen and sulfur. When amounts in excess of this cleansing requirement are added, the manganese begins to act as a hardener, 2 per cent making the iron quite hard. Steel having a manganese content of from 2 to 6 per cent and a carbon content less than 0.5 per cent is so brittle that it can be powdered under a hand hammer. When, however, more than

6 per cent of manganese is present, this brittleness disappears until 12 per cent manganese is reached. At this composition, the original toughness is restored.

27.7. Alloy Steels

With the development of the automobile industry, there arose the need for special steels that would withstand shocks and strains, resist corrosion, retain hardness at high temperatures, etc. These needs were met by the fabrication of alloy steels having the desired properties and, as these alloys became available in quantity, they rapidly came into use in all phases of industry. Metals commonly alloyed with steel include nickel, tungsten, chromium, vanadium, columbium, tantalum, molybdenum, cobalt, copper, and manganese. These metals may be added singly or in combination. So vast have become the number and variety of these alloy steels that space does not permit here any discussion of individual cases. For purposes of illustration, a few of the better known alloys are listed in Table 37, together with their composition, and a brief indication of their properties and uses.

TABLE 37

ALLOY STEELS

Name	Alloyed metal(s),	Properties	Uses
Stainless steel......	Cr (15)	Resistant to corrosion	Manufacture of ornamental parts of autos, etc.
Nickel steel........	Ni (2–5)	Stainless, very hard, yet elastic	Gears, shafting, wire rope
Invar steel.........	Ni (36)	Nonexpanding	Clocks, pendulums, tapelines, etc.
Manganese steel....	Mn (10–18)	Very hard; resists abrasive wear	Safes, railroad frogs, teeth on elevator dredges
Tungsten steel......	W (10–20) Cr (4–8)	Remains hard at high temperatures	Cutting tools, high-speed drills
Chrome-vanadium steel............	Cr (1–9) V (0.15–0.2)	Resists fatigue, has high tensile strength	Auto parts: springs, axles, etc.
Chrome-nickel steel.	Ni (1–5) Cr (1–2)	Great hardness; high tensile strength	Armor plate for battleships and tanks
Molybdenum steel..	Mo (0.3–3)	Hard, heat-resistant	Axles
Chrome steel.......	Cr (2–4)	Very hard; resistant to shock	Files, ball bearings, safes, etc.

27.8. Corrosion of Metals and Alloys

The corrosion or rusting of iron, steel, and other metals is a matter of great economic importance. Millions of dollars are spent each year in the replacement of metals damaged by corrosion. The nature of the chemical changes that occur during corrosion is not fully understood, and several theories have been advanced in an effort to provide an explanation that might lead to the development of new and better methods of control. Of the older theories, one held that corrosion of iron, for example, consists simply of the direct union of iron and oxygen; another held that corrosion results from the reaction between iron and an acid (usually carbonic acid). The presently popular *electrolytic theory of corrosion* is probably the best yet advanced, although not entirely satisfactory. This theory is too involved for complete discussion here, and for present purposes it is sufficient to indicate that, in terms of this theory, the changes that occur during rusting are likened to those which occur in battery cells (Chap. XXIII). If the supply of oxygen is unlimited, the cell reactions are

$$\begin{aligned} (-)\ \text{Terminal:}&\quad Fe^0 - 2e^- \rightarrow Fe^{++} \\ (+)\ \text{Terminal:}&\quad \tfrac{1}{2}O_2^0 + 2e^- + H_2O \rightarrow 2OH^- \\ \hline \text{Battery:}&\quad Fe^0 + \tfrac{1}{2}O_2^0 + H_2O \rightarrow Fe^{++}(OH)_2^- \end{aligned}$$

or

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{++}(OH)_2^-$$

The ferrous hydroxide is subsequently oxidized (wholly or in part) to ferric hydroxide [$Fe(OH)_3$]. If, on the other hand, oxygen is not available, the corrosive action becomes analogous to the interaction of iron and an acid, and the battery cell rections are

$$\begin{aligned} (-)\ \text{Terminal:}&\quad Fe^0 - 2e^- \rightarrow Fe^{++} \\ (+)\ \text{Terminal:}&\quad 2H^+ + 2e^- \rightarrow H_2^0 \\ \text{Battery:}&\quad Fe^0 + 2H^+ \rightarrow Fe^{++} + H_2^0 \end{aligned}$$

As a result of extensive experimentation and as an outgrowth of the various theories that have been advanced, methods have been devised whereby corrosion may be caused to occur less rapidly or in some cases prevented entirely. Any one or any combination of the following methods may be employed: (*a*) Elimination of contact with oxygen by the application of protective coatings of grease, metals (Sec. 27.9), plastics such as Bakelite, or rust-inhibiting paints. Paint pigments having rust-inhibiting properties include Pb_2OCrO_4, Cr_2O_3, $ZnCrO_4$, Pb_3O_4, and $PbSO_4$. (*b*) Protection from contact with acids. For example, before use in steam boilers, water should be treated with a base to neutralize any acid present. (*c*) Removal of electrolytes.

Water containing dissolved electrolytes corrodes metals more rapidly than pure water. (*d*) Removal of impurities. The presence of certain impurities has been found to accelerate the rate of corrosion of metals and alloys. (*e*) Removal of mechanical strains. Rate of corrosion is generally increased by deformation or mechanical strains in metals. It is a familiar fact that a bent iron nail will rust most readily at the bend.

27.9. Metallic Protective Coatings

Reference has already been made to the practice of placing protective coatings of other metals upon the surface of objects made of iron or steel by the process of electrolysis (Sec. 22.3). The same end may be accomplished also by methods not involving the use of the electric current.

Galvanizing. The process of galvanizing consists in placing a protective coating of *zinc* upon the surface of iron. Before application of the zinc, the iron must be cleaned of rust or scale by treatment with dilute sulfuric acid, a process known as *pickling*, which, incidentally, produces important quantities of hydrated ferrous sulfate ($FeSO_4 \cdot 7H_2O$) (copperas), as a by-product.

$$FeO + H_2SO_4 + 6H_2O \rightarrow FeSO_4 \cdot 7H_2O$$

The iron is then immersed in molten zinc, withdrawn, and allowed to cool, whereupon the zinc crystallizes in the characteristic spangled design. To provide protection from rusting, the quantity of zinc retained on the surface of the iron should be not less than 2 oz. per sq. ft.

Zinc is frequently applied to the surface of iron or steel by other methods. In the *Schoop process*, molten zinc is sprayed onto the surface by a blast of air in a manner similar to that used in spraying paint. In addition to metals, objects made of wood, leather, paper, etc., may be coated with zinc by this process. In the process of *sherardizing*, iron is covered with a thin layer of zinc "dust" (Sec. 26.7) at temperatures within the range of 700° to 800°C. Under these conditions, zinc penetrates the surface of the iron to a considerable extent.

Iron coated with zinc is effectively protected from corrosion. Zinc itself does not corrode appreciably since the surface oxidation of zinc produces a thin and very adherent film of zinc oxide which, in turn, protects the underlying zinc metal.[1] Should the zinc coating become

[1] Since the oxides and hydroxides of iron are also insoluble, it would seem that these corrosion products might similarly prevent the further corrosion of iron. That such is not the case may be explained readily. Whereas zinc oxide forms a

imperfect by cracking or abrasion, iron becomes exposed to a moist atmosphere containing carbon dioxide. This is equivalent to having the two metals, zinc and iron, immersed in dilute carbonic acid solution. This combination constitutes a galvanic battery cell and, since zinc is the more active of the two metals, zinc will dissolve (corrode) preferentially. Consequently, the iron is protected from corrosion so long as the zinc coating is present.

Tin Plate. Immersion of pickled iron or steel in molten tin results in the material known as *tin plate*, from which cans, caps, pails, pans, etc., are made. The objective of tin-plating is to obtain a very thin coating of tin and one which is *free from cracks, holes, or other imperfections.* The reason for this latter requirement becomes clear if one considers the nature of the galvanic battery cell involving the two metals, iron and tin. Since iron is more active than tin, an imperfection in a coating of tin results in preferential corrosion of iron; hence, an *imperfect* tin-plating, rather than providing protection from corrosion, actually promotes corrosion and is worse than no coating at all.

In addition to zinc and tin, and aside from those metals applied by electrolysis, other metals commonly applied as protective coatings include lead and cadmium. Both of these metals are applied by immersion as in the case of zinc or tin. Lead is commonly used as a protective coating on wire, cables, steel shingles, etc., while cadmium is (less frequently) used as a coating on numerous automobile parts, laboratory apparatus, etc. Although objects plated with cadmium present a more attractive appearance, the extensive use of this metal is retarded by its relatively high cost and limited production.

EXERCISES

1. If, instead of hematite, one wished to use (*a*) siderite, or (*b*) pyrite as a source of iron, how might these ores have to be treated before introduction into the blast furnace? Write equations for the reactions involved.

2. Write equations representing the reactions that occur when hematite is reduced to elemental iron in the blast furnace. In each case, indicate the approximate temperature at which the reaction occurs.

3. Assuming that an iron ore consists of 70 per cent Fe_2O_3 and 30 per cent SiO_2, calculate (*a*) the maximum number of tons of iron that could be produced from 1 ton of this ore and (*b*) the weight of limestone (in pounds) that would be required to convert into slag the silicon dioxide present in 1 ton of the ore.

4. Define the following terms: (*a*) pig iron, (*b*) white cast iron, (*c*) gray cast iron, (*d*) malleable cast iron, (*e*) steel, (*f*) slag, (*g*) pickling, (*h*) galvanizing, (*i*) sherardizing, (*j*) cementite, (*k*) spiegeleisen, (*l*) copperas.

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very firm adherent film on the surface of zinc, the insoluble corrosion products of iron are flaky and *porous* and hence do not effectively prevent further attack of the underlying metallic iron.

5. For each of the following processes, list the raw materials required and the primary product of the process: (*a*) the open-hearth process, (*b*) the Schoop process, (*c*) the cementation process, (*d*) the Bessemer process, (*e*) the crucible process.

6. What is the essential difference between (*a*) wrought iron and steel, (*b*) the acid Bessemer and the basic Bessemer process?

7. In comparison with the Bessemer process, what advantages are involved in the use of the open-hearth process?

8. In the United States, the richest iron-ore deposits are located in the Lake Superior region. In view of this fact, how may one explain that great centers of steel production are located in Indiana, Ohio, West Virginia, and Pennsylvania?

9. Why is it that the Birmingham, Ala., area is the only one in which iron ore is both mined and smelted?

10. List the factors that one should take into account in efforts to prevent, or to decrease the rate of, corrosion of iron or steel.

11. If a crack or other imperfection occurs in a coating of lead on iron, which of these metals will corrode the more rapidly? Justify the answer given.

12. What are the chief by-products of the production of iron? How are these by-products used?

13. Compare the mechanical properties of cast iron, wrought iron, and steel.

14. If pig iron having a relatively high phosphorus content were converted to steel by the acid Bessemer process, what would be the properties of the resulting product?

15. What properties are imparted to iron by each of the following impurities: (*a*) manganese, (*b*) carbon, (*c*) sulfur?

SUGGESTED READING

Journal of Chemical Education

Burchard, The Sources of Our Iron Ores, **10**, 195, 288 (1933).

Franklin, A Brief Lesson in the Chemistry of Pig Iron, 8, 143 (1931).

Crook, Alloy Steels and Their Uses, 4, 583 (1927).

Pethybridge, Modern Heat Treating Practices, **21**, 152, 204 (1944).

Rohrman, Corrosion, the Billion Dollar Thief, **10**, 141, 215, 297 (1944).

Blum, Protection against Corrosion by Means of Metallic Coatings, **4**, 1477 (1927).

Rogers, Modern Methods of Metal Finishing, **14**, 57 (1937).

Industrial and Engineering Chemistry

Wachter and Smith, Preventing Internal Corrosion of Pipe Lines, **35**, 358 (1943).

CHAPTER XXVIII

SOME NONMETALLIC ELEMENTS

From the study of the periodic arrangement of the elements (Chap. XIII), the student will recall that only a relatively small number of the stable chemical elements may be considered as predominantly nonmetallic in character. This fact, however, should not lead one to assume that these elements are of only secondary importance. From the standpoint of future developments it is further significant that, in all probability, no additional nonmetals remain to be discovered.

Some attention has already been devoted to the study of several of the nonmetals, including oxygen (Chap. IV), hydrogen (Chap. VIII), and the inert gases of the atmosphere (Sec. 4.6). With this background, the present discussion will involve a summarization of those chemical and physical properties which are shared in some degree by all of the nonmetallic elements and a brief delineation of the chemistry of several additional nonmetallic elements, *viz.*, carbon, silicon, nitrogen, phosphorus, and sulfur. The properties of the elements of the halogen family will be considered in a separate chapter.

28.1. Physical Properties of Nonmetals

Of the predominantly nonmetallic elements, seven are solids (B, C, Si, P, S, Se, I) under ordinary atmospheric conditions, only one is a liquid (Br), and the remainder (H, N, O, F, Cl, He, Ne, A, Kr, Xe) are gases. The physical properties of these elements present far more striking contrasts than do those of the metals (Sec. 25.4). Thus, among the nonmetals one encounters the extremely volatile helium which *boils* at $-267°C.$ (*i.e.*, just 5° above the absolute zero) and the nonvolatile element carbon which melts at about 3500°C. Similarly, the densities and other physical properties of these elements differ tremendously, as will be made more evident by an inspection of the table of physical properties of the elements given in the Appendix.

Allotropy. Particularly among the nonmetals that are solids under ordinary atmospheric conditions, it is frequently found that the same element is capable of existing in different physical forms. Thus, the element carbon may exist as the crystalline diamond or the amor-

phous wood charcoal. Although these elements exhibit striking differences in physical properties, their chemical properties are usually not significantly different. If, for example, one should burn samples of diamond and wood charcoal in an excess of oxygen, the reaction product in both cases would be carbon dioxide and the two samples of carbon dioxide would be found to be identical in all respects. The only important difference involved is the magnitude of the accompanying energy change. These different physical forms of the same element are known as *allotropic forms* or *allotropic modifications*. Although allotropy is also encountered among the metals, the best-known examples of this phenomenon are to be found among the nonmetals and several examples will be discussed in the following pages.

28.2. Chemical Properties of Nonmetals

With the exception of the inert gases, most of the nonmetallic elements have four or more electrons in their outermost orbits. The atoms of these elements tend to gain electrons to form negative ions and, as a consequence, the nonmetallic elements in their various forms of chemical combination usually exist as simple or complex anions. Electrons gained by these atoms are held by the attraction of the positive nucleus and the firmness with which these electrons are held differs from one nonmetal to another. Since an element that has gained one or more electrons may be said to be in an *electronegative* condition, it follows that, to the extent that nonmetals differ in their tendencies toward acquisition of electrons, these elements exhibit different degrees of electronegativity. Thus, just as the metals differ in their tendencies toward loss of electrons, so the nonmetals differ in the opposite direction.

In this connection, it should be recalled that the nonmetals in general (as well as many of the less electropositive metals and the metalloids) show pronounced tendencies toward compound formation as a result of sharing of electrons (Sec. 15.5). Another property shared generally by all the nonmetals (except the inert gases) is that of variable valence. The student need only recall the study of the various states of oxidation exhibited by elements such as nitrogen and sulfur (Secs. 24.3 and 24.4) to appreciate the extent to which variable valence is encountered among typical nonmetals. Finally, it should be recalled that the nonmetals include those elements whose binary compounds with oxygen (*e.g.*, SO_3, P_2O_5, etc.) or hydrogen (*e.g.*, HCl, HBr, H_2S, etc.) react with water to form acidic solutions. Thus, the nonmetals are properly designated as the acid-forming elements.

CARBON

Three of the principal sources of carbon are coal, petroleum, and natural gas. Thus, the greater part of the world's available fuel resources has consisted of compounds of carbon. Similarly, all forms of plant and animal life involve carbon compounds, many of which are exceedingly complex. The element carbon is unique in the extent to which it combines with a few other elements to form a wide variety of compounds. Several hundred thousand compounds are known already, and many more are being produced each day in chemical laboratories throughout the world.

28.3. Allotropic Forms of Carbon

In the solid state, the element carbon exists in three different allotropic modifications, *viz.*, amorphous carbon, and the two crystalline forms known as *diamond* and *graphite*. Amorphous carbon includes numerous common products such as wood charcoal, boneblack, coke, lamp black, and carbon black. Each of these varieties of crystalline and amorphous carbon possesses properties that render it useful for a variety of purposes.

Diamond. The chief sources of the diamond are the Kimberley region in South Africa, Brazil, and the East Indies. The diamond crystal is cubic, its density is 3.5, and, although it is the hardest substance known to occur in nature, it is brittle and easily shattered. The diamond has an unusually high melting temperature (3500°C.), does not act as a conductor of electricity, and is so inert chemically that the combustion of carbon in oxygen to form carbon dioxide does not occur until a temperature of about 800°C. is reached. Through the study of the crystalline structure of the diamond by means of X rays it has been found that the carbon atoms in the crystal are arranged in tetrahedral form (Fig. 120), each atom being equidistant from the four other carbon atoms surrounding it.

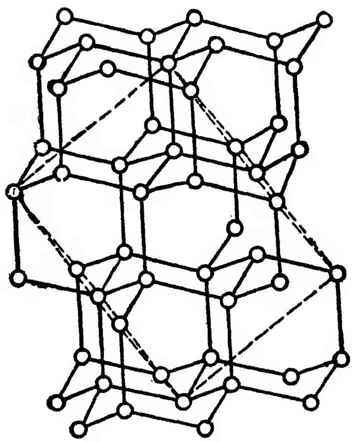


FIG. 120.—The diamond lattice. (*Courtesy of Seitz, Modern Theory of Solids, McGraw-Hill Book Company, Inc.*)

The chief uses of the diamond depend largely upon the properties of hardness and ability to refract light. Diamonds that are trans-

parent and largely free from impurities that impart discoloration are used primarily as gem stones. Diamonds that are variously colored (mostly black) are used in polishing, glass cutting, and in the construction of the cutting edges of rock drills, rock-cutting saws, etc. Many attempts have been made to produce diamonds in the laboratory, but none of these efforts has met with other than very limited success.

Graphite. This crystalline form of carbon is found in Ceylon, Siberia, Madagascar, and in various regions in central Europe and the United States, Canada, and Mexico. The melting temperature of graphite is the same as that of diamond, and these two forms of elemental carbon are also similar in their low degree of chemical activity. In contrast to the diamond, however, graphite has a relatively low density (2.25) and is a good conductor of electricity. As shown in Fig. 121, the crystal structure of graphite is markedly different from that of the diamond and involves carbon atoms arranged in planes of hexagonal ring structure. When diamond is heated to 3500°C., it vaporizes rapidly and, upon cooling, the vapors condense (solidify) in the form of graphite.

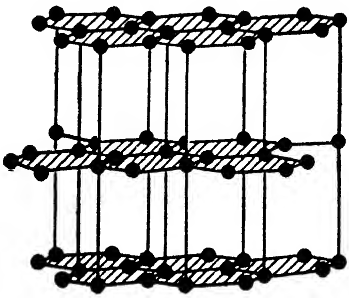


FIG. 121.—The graphite lattice. (*Courtesy of Seitz, Modern Theory of Solids, McGraw-Hill Book Company, Inc.*)

Although much graphite is readily available in nature, large quantities of graphite, which is superior to the naturally occurring material, are manufactured artificially by a process invented by the American chemist, Acheson. In the *Acheson process*, powdered anthracite coal is heated between graphite electrodes in an electric furnace for about twenty hours. As shown in Fig. 122, a core of granulated carbon is placed in the center of the charge between the two electrodes since the powdered coal alone is a very poor conductor. To exclude air, the charge in the furnace is covered with a layer of sand and carbon. Utilizing a current of about 200 amp. at 40,000 to 50,000 volts, the temperatures produced within the charge are sufficient to volatilize the impurities and to convert the carbon (from the coal) into graphite of about 99.5 per cent purity.

Graphite is used in the manufacture of electrodes for high-temperature furnaces, crucibles, "lead" pencils, pigments, etc. Colloidal suspensions of graphite in water, oil, or grease are commonly employed as lubricants. The planar leaflike structure of graphite is such that the layers in the crystal lattice may easily slide over one another, and

the greaselike properties of graphite make this material particularly useful in the elimination of friction.

As indicated previously, the so-called *amorphous* varieties of carbon embrace numerous common materials. It is perhaps improper to designate all these materials as truly amorphous. Some of these materials contain less well-defined crystalline structures comparable to that of graphite but with a much less well-ordered and regular orientation of carbon atoms. Nevertheless, these materials have long been known as forms of amorphous carbon.

Wood Charcoal. In addition to a rather wide variety of other products (Sec. 35.4) wood charcoal is produced by heating wood, nut shells, etc., in the presence of a limited supply of oxygen. This operation is commonly known as *coking* or *destructive distillation.* After all the volatile products have been removed, the residue amounts to

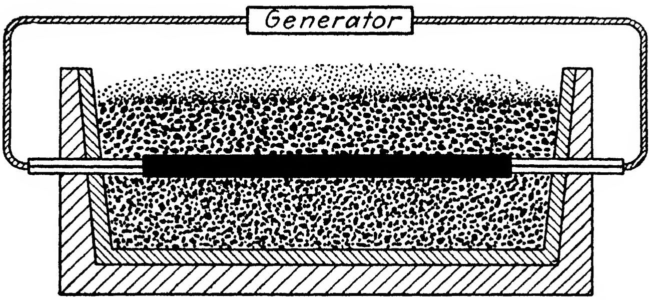


FIG. 122.—Electric furnace for the production of graphite by the Acheson process.

about 20 per cent of the original weight of wood and consists of about 97 per cent carbon. The remaining 3 per cent is made up of nonvolatile minerals present in the wood. The chief use of charcoal is found in the iron and steel industry but, in addition, significant quantities are used as a fuel in the form of briquettes or in powdered form. Some wood charcoal is employed as a material for filtering rain water and as a low-temperature absorbent for certain vapors. Cocoanut charcoal is used to absorb poisonous gases in gas masks.

Boneblack. By heating "green" bones, one obtains a nonvolatile residue known as *boneblack* or *animal charcoal.* This product contains only about 10 per cent of finely divided carbon uniformly distributed throughout a porous mass of (principally) calcium phosphate. Because the carbon in this product has the ability to adsorb many colored compounds, it serves as an excellent decolorizer for sugar sirups, as well as many other colored and turbid solutions.

Coke. Just as the destructive distillation of wood yields wood charcoal and volatile products, so the heating of bituminous coals

results in a wide variety of useful volatile materials (Sec. 35.3) and amorphous carbon in the form known as *coke*. The chief uses of coke are in connection with the iron and steel industries, but important quantities of this form of carbon are also used as a fuel in other industries and in the home.

Lamp Black. A relatively pure and very finely divided form of amorphous carbon known as *lamp black* is produced by burning light oils (which are rich in carbon) in a limited supply of air. The soot is collected in settling chambers upon coarse cloth screens through which the smoke must pass. Lamp black is used in the manufacture of inks, paints, stove polish, crayons, carbon paper, etc.

Carbon Black. This material is also nearly pure carbon and is produced by the incomplete combustion of natural gas. This process is exceedingly wasteful. Although the burning of 1000 cu. ft. of natural gas should theoretically yield 30 lb. of carbon black, a yield of only about 1½ lb. is ordinarily obtained. This finely divided variety of carbon is used in very large quantities as a filler in the manufacture of automobile tires and other rubber goods. Carbon black is also used in the manufacture of phonograph records, printing inks, and certain types of lacquers.

SILICON

In comparison with carbon, the related element silicon is relatively unimportant, so far as uses for the uncombined element are concerned. Most of the silicon produced commercially is used in the metallurgical industries either as such or in connection with the manufacture of a useful iron-silicon alloy known as *ferrosilicon*. It is rather surprising that one of the most abundant of all the elements should find so few commercial applications.

28.4. Preparation and Properties of Silicon

Elemental silicon of about 98 per cent purity may be produced by the reduction of silicon dioxide by aluminum.

$$3SiO_2 + 4Al \rightarrow 3Si + 2Al_2O_3$$

The crude silicon is then dissolved in molten aluminum, cooled, and the aluminum dissolved by dilute hydrochloric acid. There remains elemental silicon in a crystalline form similar to that of the diamond.

Silicon is a very hard but brittle element having a melting temperature of 1422° and a density of 2.40. This element is fairly reactive toward the halogens and solutions of strong bases such as potassium hydroxide. Silicon reacts less readily with oxygen to form silicon

dioxide and with other elements similarly to form a class of binary compounds known as *silicides.*

NITROGEN

In relation to the vital processes of all living forms of matter, only a few elements are more widely utilized than nitrogen. Directly or indirectly, all forms of plant and animal life are dependent upon the availability of nitrogen in the form of its compounds. Although large deposits of nitrogen compounds are found in nature, *e.g.*, the extensive deposits of sodium nitrate (commonly known as *Chile saltpeter*) which are found in Chile, Argentina, Peru, Bolivia, California, and elsewhere, these supplies are inadequate to permit the maintenance of soil fertility and the continuation of presently existing forms of life. It is therefore necessary to utilize in some way the available supplies of nitrogen in the atmosphere.

28.5. Fixation of Atmospheric Nitrogen

Nitrogen gas constitutes about four-fifths of the atmosphere; hence, tremendous supplies of this element are available. Elemental nitrogen may be converted into compound forms by several methods. Although animals cannot utilize atmospheric nitrogen directly, certain plants can do so. The bacteria that live in the nodules (Fig. 123) on the roots of legumes such as peas, beans, and clover are able to convert atmospheric nitrogen into forms that can be utilized by the plants with which these bacteria are associated. Some atmospheric nitrogen also becomes "fixed" through the agency of electric discharges (lightning) during thunderstorms. In these discharges, atmospheric nitrogen and oxygen combine to form oxides of nitrogen which dissolve in the falling drops of rain and are thereby imparted to the soil. It is a surprising fact that the quantity of nitrogen made available in this manner amounts to more than 5 lb. per acre per year. In addition to the foregoing methods, several artificial processes for the fixation of atmospheric nitrogen have been devised and are used extensively. These will be discussed in some detail in the next chapter.

28.6. Preparation of Nitrogen

The preparation of pure nitrogen on a laboratory scale is best accomplished by the formation and subsequent decomposition of ammonium nitrite. These reactions are effected in aqueous solution by warming the reactants *cautiously.*

$$NH_4^+Cl^- + Na^+NO_2^- \rightarrow Na^+Cl^- + NH_4^+NO_2^-$$
$$NH_4^+NO_2^- + \text{heat} \rightarrow N_2 + 2H_2O$$

Pure nitrogen is also formed when gaseous ammonia is passed over heated copper oxide and the resulting gaseous mixture is dried.

$$3CuO + 2\overline{N}H_3 \rightarrow 3Cu + 3\overline{H_2O} + \overline{N}_2$$

Nitrogen may also be produced directly from air by the fractional distillation of liquid air (Sec. 6.2) or by passing air over heated copper.

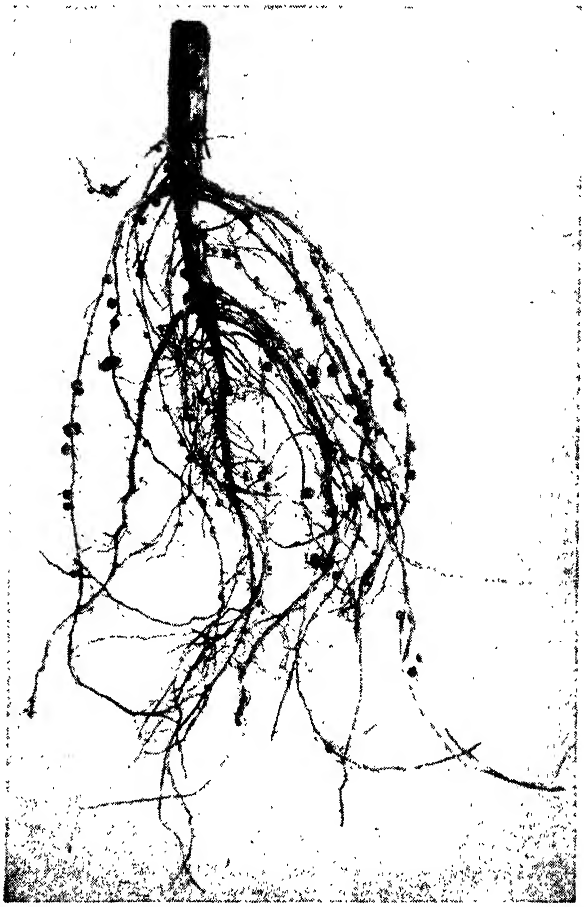


FIG. 123.—Soybean roots with nodules that contain nitrogen-fixing bacteria. (*Courtesy of U.S. Dept. of Agriculture, Bureau of Plant Industry.*)

In the latter case, oxygen is removed by combination with the copper to form copper oxide, but the resulting nitrogen is not entirely pure since it is contaminated by the inert gases present in the original sample of air.

28.7. Properties and Uses of Nitrogen

Pure gaseous nitrogen is tasteless, odorless, colorless, and does not support combustion. This gas is slightly lighter than air, 1 liter weighing 1.25048 g. under standard conditions of temperature and pressure. The very slight solubility of nitrogen in water is shown by the fact that, at 25°C., 100 g. of water will dissolve only 0.0019 g. of nitrogen. Solid nitrogen melts at −209.8°C., and the pure liquid boils at −195.8°C.

Chemically, the element nitrogen is somewhat unreactive. Under appropriate conditions, however, it combines with hydrogen to form several hydrides, the most important of which is the gas ammonia (NH_3). Nitrogen also combines with oxygen to form several different oxides (*e.g.*, N_2O, NO, N_2O_3) and with other nonmetals and metals to form a class of binary compounds known as *nitrides*, *e.g.*, S_4N_4, AlN, Mg_3N_2, etc.

The large-scale uses of nitrogen are those involving the commercial production of nitrogen compounds such as nitric acid, ammonia, and cyanamide (Sec. 29.10). Although appreciable quantities of nitrogen are used in a process known as *nitriding* which is employed in the hardening of steel, gaseous ammonia has come into use recently as the source of nitrogen required for this process.

PHOSPHORUS

It is an interesting fact that the two elements most necessary in the maintenance of soil fertility are the related elements nitrogen and phosphorus, which occupy adjacent positions in periodic Group V. Phosphorus occurs in nature only in the combined form, chiefly as the mineral *phosphorite* [$Ca_3(PO_4)_2$]. Impure calcium phosphate, known as *phosphate rock*, is mined extensively in Tennessee, Florida, Montana, and Idaho. Large deposits of this mineral are also found in Morocco and Tunisia in North Africa.

28.8. Allotropic Forms of Phosphorus

Solid phosphorus exists in two distinct allotropic modifications and is also commonly encountered in a form consisting of a mixture of the two. *White* (or yellow) *phosphorus* is a translucent, waxlike solid which melts at 44°C., boils at about 290°C., and has a density of 1.83. When vaporized, the resulting gas consists of tetra-atomic molecules (P_4) up to a temperature of about 1500°, whereupon these molecules partly dissociate into (and exist in equilibrium with) diatomic molecules (P_2). White phosphorus is insoluble in water but is soluble in

solvents such as ethyl ether and carbon disulfide. Great care should always be exercised in handling this form of phosphorus since it is highly inflammable and very poisonous. Skin burns caused by phosphorus are very slow to heal and exceedingly painful.

When white phosphorus is heated above 250°C. in the absence of air and in the presence of a trace of iodine which serves as a catalyst, the white modification is *incompletely* converted to *violet phosphorus.* Since this conversion is seldom complete, the resulting amorphous material consists of the white and violet allotropes and because of its brownish-red appearance is known as *red phosphorus.* Relatively little is known about the nature of violet phosphorus. It is best prepared by heating white phosphorus under high pressures or by crystallization from molten lead. Violet phosphorus has a metallic appearance, is noninflammable, and has a density of 2.69.

Because it is a mixture, the physical properties of red phosphorus are variable. Thus, the density ranges from 2.10 to 2.34, depending upon the completeness of the transformation from the white to the violet modification. The vapor formed when red phosphorus is heated is identical with that from white phosphorus; in either case, condensation of these vapors produces white phosphorus. The red modification is much less active chemically than the white variety and is insoluble in those solvents which dissolve white phosphorus.

28.9. Preparation and Uses of Phosphorus

The preparation of elemental (white) phosphorus is carried out in an electrically heated furnace into which a mixture of phosphate rock, sand, and coke is fed continuously by means of a screw conveyer.

$$2Ca_3(PO_4)_2 + 10C + 6SiO_2 \rightarrow P_4 + 10\overline{CO} + \underline{6CaSiO_3}$$

The phosphorus vapor distills out of the furnace and is liquefied in a condenser, after which the liquid is filtered and cast into sticks in molds immersed in water. The molten calcium silicate is withdrawn from the bottom of the furnace and solidified as a slag.

The greater part of the elemental phosphorus produced in this country is used in the manufacture of a type of alloy known as *phosphor bronze.* In chemical warfare, smoke screens have been produced by the ignition (by reaction with atmospheric oxygen) of white phosphorus liberated from shells, grenades, or bombs. Dense clouds of white smoke were formed owing to oxidation of phosphorus to form finely divided particles of P_2O_3 and P_2O_5. Burning white phosphorus is also useful as an antipersonnel weapon. Another important application for phosphorus lies in its use in the production of phosphorus

sesquisulfide (P_4S_3) which is used in the manufacture of matches, and in the production of other compounds of phosphorus. The chief use of the "red" modification of this element is also in the manufacture of matches.

Matches. For many years, matches were made by dipping sticks of wood into a paste made of glue, lead dioxide, and white phosphorus. Long exposure to white phosphorus sometimes causes horrible diseases of the bones. For this reason and because of the constant fire hazard, the use of white phosphorus in the manufacture of matches is prohibited by law. The modern strike-anywhere match has a head consisting of a mixture of potassium chlorate, paraffin, glue, and finely ground glass. The tip of the match head also contains some phosphorus sesquisulfide (P_4S_3). Ignition of the P_4S_3 by friction initiates combustion, which then extends to the $KClO_3$, the paraffin, and finally to the wood. In the case of the safety match, a side of the matchbox is coated with a mixture of red phosphorus, ground glass, and glue. The head of the match is a mixture of potassium chlorate (the source of oxygen), antimony trisulfide (Sb_2S_3) (the combustible material), and glue. Thus, the head of the match contains no phosphorus or sesquisulfide, and such a match can be ignited readily only by friction against the side of the box bearing the red phosphorus which ignites the materials in the match head.

SULFUR

Attention has already been directed toward the generality and extent of the occurrence of sulfur in the form of simple and complex sulfides of the heavy metals (Sec. 25.1). Of greater consequence, however, are the vast underground deposits of nearly pure elemental sulfur found in the Gulf coast areas of Louisiana and Texas. Less extensive and less pure deposits of elemental sulfur are also found in a number of other countries, principally Sicily, Spain, Chile, Mexico, and Japan.

28.10. Mining of Sulfur

In Sicily, sulfur occurs as crystalline deposits disseminated in porous limestone and gypsum. After underground or open-pit surface mining, the crude sulfur-bearing ores are crushed and then treated in the Calcarone furnace. Such a furnace consists of a large vertical cylindrical masonry structure having a sloping bottom. The charge is ignited at the top, and the rate of burning is regulated so as to use the minimum amount of sulfur to produce the heat necessary to melt the remainder. Nevertheless, from 30 to 35 per cent of the available

sulfur is burned to sulfur dioxide. The molten sulfur flows down the sloping bottom to an opening where it is cast into molds. This rather impure product is the common commercial material known as *brimstone.* To remove impurities such as arsenic and selenium, this crude sulfur must be purified by distillation.

The crude sulfur-bearing ores of Japan are charged into furnaces and the sulfur is distilled out; the resulting vapors are liquefied and cast into "mats" of solid sulfur.

Frasch Process. In the United States, elemental sulfur is made available by the ingenious *Frasch process* (Fig. 124). A well is drilled into the sulfur-bearing rocks which occur at an average depth of about 1000 ft. but which may be at depths as great as 1600 to 2000 ft. A 10-in. surface casing is cemented into the cap rock to block off the loose overlying formations. The well is then equipped with three concentric pipes, one of which is a 6-in. hot water (steam) pipe, the second is a 3-in. sulfur line, and the third is a 1-in. compressed-air line. Steam heated to 160° to 170°C. and forced under pressure through the 6-in. pipe into the well serves to melt the sulfur. Compressed air under a pressure of 500 lb. per sq. in. is sent into the well through the 1-in. pipe. Air bubbles become trapped in the molten sulfur and render the liquid sulfur-water mixture lighter and therefore easier to force to the surface (through the 3-in. pipe) by the pressure supplied by the compressed air. At the surface, the molten sulfur flows into metering tanks (Fig. 125) and then is pumped through steam-jacketed pipes to a central solidification vat (Fig. 126). Such vats hold from 400,000 to 750,000 tons of sulfur of an average purity of 99.50 per cent and a maximum purity of 99.95 per cent. A single well may deliver as much as 400 to 600 tons per day.

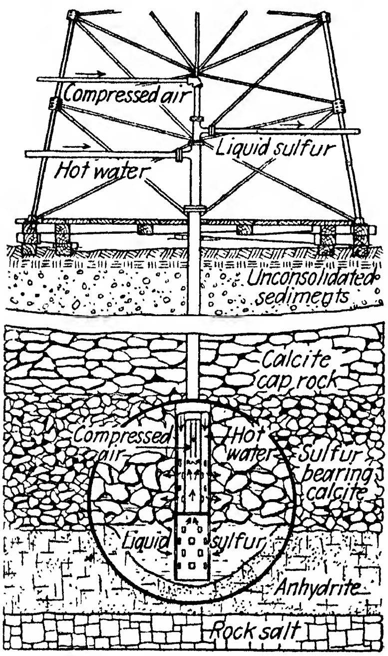


FIG. 124.—Diagram showing the piping of a sulfur well. (*Courtesy of Texas Gulf Sulfur Company.*)

The development of the Frasch process, first used successfully in 1891, has made this country substantially independent of foreign

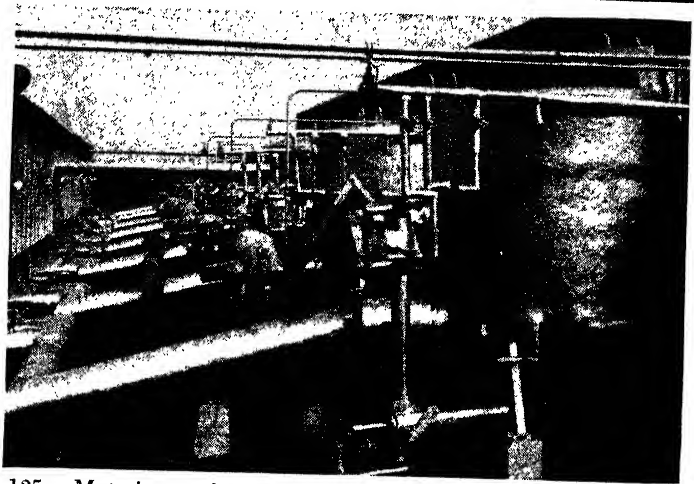


FIG. 125.—Metering tanks used in measuring the production of sulfur from each well. Each tank has a capacity of ten tons. (*Courtesy of Texas Gulf Sulfur Company.*)

FIG. 126.—Photograph showing discharge of molten sulfur into a solidification vat and a mass of solid sulfur in the background. (*Courtesy of Texas Gulf Sulfur Company.*)

sources of sulfur. An inspection of Table 38 shows the growth of this country as a producer of sulfur (in relation to world production) and the rapid decline in the quantity of sulfur imported.

TABLE 38*
PRODUCTION OF SULFUR IN METRIC TONS

Year	United States imports	United States production	World production
1895	126,760	1,676	398,916
1900	167,328	4,630	581,282
1901	175,310	6,977	604,930
1902	176,951	7,565	552,996
1903	190,931	35,660	631,035
1904	130,421	196,588	767,249
1905	84,579	218,440	830,609
1910	30,544	259,699	787,732
1915	24,647	299,133	860,000
1920	44	1,542,059	1,941,052
1925	102	1,431,912	2,213,330
1930	29	2,558,981	3,091,709
1935	1,763	1,632,590	2,254,000
1939	14,000	2,091,000	2,900,000

* Courtesy of BADGER and BAKER, "Inorganic Chemical Technology," McGraw-Hill Book Company, Inc., New York, 1941.

28.11. Allotropic Forms of Sulfur

Solid sulfur exists in two crystalline modifications. *Rhombic* sulfur consists of S_8 molecules, is stable at temperatures below 95.5°C., has a specific gravity of 1.96, and is soluble in carbon disulfide. At 95.5°C., rhombic sulfur changes slowly with absorption of heat, into the *monoclinic* form. *Molten* rhombic or monoclinic sulfur also consists of S_8 molecules which exist as a pale yellow, thin, and limpid liquid known as λ-sulfur. When the temperature is raised, λ-sulfur is slowly converted to dark and viscous μ-sulfur which consists of S_6 and S_4 molecules and which is considered to be the amorphous variety of sulfur. In carbon disulfide, λ-sulfur is soluble and μ-sulfur is insoluble; thus a separation of the two forms is permitted.

When liquid sulfur that has been heated extensively above its melting temperature is chilled suddenly, there is obtained a mass of "plastic" sulfur which owes its plasticity to its high content of μ-sulfur. If sulfur is sublimed (Sec. 1.9), the vapors condense in the form of very fine and usually very pure crystals known as *flowers of sulfur*.

28.12. Uses of Sulfur

In the elemental form, sulfur is used (*a*) in the vulcanization of rubber, (*b*) in the manufacture of black powder, (*c*) as a fungicide (in powder form) particularly in the growing of grapes, and (*d*) as "lime-sulfur" spray for fruit trees. Although the above uses require considerable amounts of this element, the great bulk of the world's production of sulfur goes into the manufacture of sulfur dioxide which may be used as such or converted to other industrially important sulfur compounds, some of which will be discussed in the next chapter.

EXERCISES

1. Give a brief summary of (*a*) the physical properties, and (*b*) the chemical properties that are generally characteristic of the nonmetallic elements.

2. If element *A* is more electronegative than element *B*, which would be the better oxidizing agent? Justify the answer given.

3. In what respect do the allotropic modifications of a given element differ most markedly?

4. Should plastic sulfur be considered as a distinct allotropic form of sulfur? Why or why not?

5. Given the possibilities of reaction between (*a*) a highly electropositive metal and a highly electronegative nonmetal, and (*b*) two highly electronegative nonmetals, which pair would more likely combine by sharing of electrons? Which pair would combine the more readily? In each case, cite arguments consistent with the answer given.

6. What raw materials are required for (*a*) the operation of the Acheson process, (*b*) the commercial production of white phosphorus, (*c*) the commercial production of elemental silicon?

7. Write equations representing the reactions involved in (*a*) the preparation of *pure* gaseous nitrogen, (*b*) the reduction of silicon dioxide by aluminum, (*c*) the liberation of phosphorus from phosphate rock.

8. List the most important uses for each of the following: (*a*) graphite, (*b*) colored diamonds, (*c*) sulfur, (*d*) red phosphorus, (*e*) nitrogen, (*f*) white phosphorus, (*g*) silicon.

9. List the raw material from which each of the following materials is produced and indicate the most important uses of each: (*a*) lamp black, (*b*) wood charcoal, (*c*) boneblack, (*d*) carbon black, (*e*) coke.

10. By what *natural* methods is the fixation of atmospheric nitrogen accomplished?

11. What bearing does the crystalline structure of graphite have upon the properties of this form of carbon?

12. In view of previous use of terms ending with the suffix, *-ide*, what would be implied by the use of the term phosphide?

13. If one used phosphate rock ore containing 26 per cent calcium phosphate in a process having an over-all efficiency of 80 per cent, what weight of phosphorus would be obtained by processing 3.5 tons of this ore?

14. Draw a simplified diagram showing the essential features of the Frasch process.

15. Give the specific names and at least one distinguishing characteristic of two allotropic forms of each of the following elements: (*a*) sulfur, (*b*) carbon, (*c*) phosphorus.

16. What volume of nitrogen (at 25°C. and 740 mm.) would be formed if 1 lb. of copper were produced by the reaction between gaseous ammonia and hot copper oxide?

SUGGESTED READING

Journal of Chemical Education

Rohrman, Non-metallics in the Chemical Industry, **14,** 353 (1937).
Helbig, Activated Carbon, **19,** 194 (1942).
Hetherington, The Fixation of Atmospheric Nitrogen, **3,** 170 (1926).
Curtis, Nitrogen Fixation, **19,** 161 (1942).
Crass, A History of the Match Industry, **18,** 116, 277, 316, 380, 428 (1941).
Siegel, Ignition of the Safety Match, **17,** 515 (1940).
Anon., Sulfur Mining, **6,** 129 (1929).
Cunningham, Sulfur, **12,** 17, 83, 120 (1935).
Harrar, Sulfur from Popocatepetl (Mexico), **11,** 640 (1934).
Schaefer and Palmer, Plastic and Allotropic Forms of Sulfur, **17,** 473 (1940).
Sheely, The Termo-allotropic Modifications of Sulfur, **18,** 30 (1941).
James, The Number of Atoms in the Sulfur Molecule, **6,** 556 (1929).

CHAPTER XXIX

SOME BINARY COMPOUNDS OF NONMETALLIC ELEMENTS

In the preceding chapter, the preparation, properties, and uses of several typical nonmetals were considered in some detail. The student will recognize that these elements are capable of forming many binary, ternary, and complex compounds and that the task of becoming familiar with all these individual substances would be a formidable one. Because only a few of these compounds warrant consideration from the standpoint of their practical utility, this chapter is concerned with the study of the more important *binary* compounds of the elements treated in the preceding chapter. Other binary and ternary compounds of nonmetals will be encountered in the study of Chaps. XXX to XXXII.

OXIDES OF CARBON

The element carbon forms three compounds with oxygen, the most common being the dioxide (CO_2). The others are the very poisonous carbon monoxide (CO) and the relatively less well-known carbon suboxide (C_2O_3).

29.1. Carbon Monoxide

The preparation of pure gaseous carbon monoxide may be accomplished by the endothermal reaction between carbon dioxide and hot carbon at elevated temperatures.

$$\overline{CO}_2 + C \rightarrow 2\overline{CO} - 41{,}500 \text{ cal.}$$

Much carbon monoxide is produced in this manner when coal or coke is used as a fuel under conditions such that the supply of oxygen is limited and carbon is present in excess. The carbon dioxide first formed reacts with the excess carbon to form the monoxide. This gas is also formed in limited quantities by the incomplete combustion of liquid fuels in internal-combustion engines.

For laboratory-scale use, the preparation of carbon monoxide is accomplished best by the thermal decomposition of formic acid or sodium formate.

$$HCOOH + \text{heat} \rightarrow \overline{CO} + H_2O$$
$$HCOONa + \text{heat} \rightarrow \overline{CO} + Na^+OH^-$$

From the first of the above equations, it is evident that carbon monoxide is the anhydride of formic acid.

Properties of Carbon Monoxide. Carbon monoxide is a colorless, odorless, and tasteless gas which is slightly lighter than air and only very slightly soluble in water. Carbon monoxide has a pronounced tendency toward combination with oxygen (to form carbon dioxide) and burns in oxygen with a bright, blue flame. Because of its affinity for oxygen, carbon monoxide is an excellent reducing agent for the reduction of oxides of the metals. The student will recall the use of carbon monoxide in connection with the metallurgy of iron (Sec. 27.2). Similarly, oxides of metals such as copper and lead are reduced when heated in the presence of carbon monoxide.

$$CuO + \overline{CO} \rightarrow Cu + \overline{CO_2}$$
$$PbO + \overline{CO} \rightarrow Pb + \overline{CO_2}$$

Carbon monoxide is an extremely toxic gas. Inhalation of air containing 1 volume of carbon monoxide in 300 volumes of air causes death in a few minutes. The hemoglobin (red coloring matter) of the blood forms an unstable union with oxygen and carries this oxygen to all parts of the body. Carbon monoxide, however, forms a very *stable* compound with hemoglobin and thus renders it incapable of performing its function as an oxygen carrier. Accordingly, death from carbon monoxide poisoning is the result of an inadequate supply of oxygen in the various parts of the body. Many lives are lost each year because of failure to provide for the elimination of carbon monoxide resulting from the incomplete burning of natural gas in home heating units, from allowing automobile engines to operate in closed garages, from explosions in mines, etc.

29.2. Preparation of Carbon Dioxide

The commercial production of carbon dioxide by the reaction between steam and either methane or hot carbon has already been described (Sec. 8.5). Carbon dioxide produced industrially as a by-product of the combustion of fuels such as coal and coke is reclaimed by reaction with aqueous sodium carbonate solution.

$$\overline{CO_2} + Na_2^+CO_3^= + H_2O \rightarrow 2Na^+HCO_3^-$$

The resulting sodium hydrogen carbonate is heated to liberate carbon dioxide gas,

$$2Na^+HCO_3^- \rightarrow Na_2^+CO_3^= + \overline{CO_2} + H_2O$$

and the sodium carbonate is used over again. Carbon dioxide is also formed as a by-product of the manufacture of lime by the thermal decomposition of carbonaceous rocks,

$$CaCO_3 + \text{heat} \rightarrow \overline{CO_2} + CaO$$

and as a by-product of certain fermentation processes used in the production of alcoholic beverages.

In the laboratory, carbon dioxide is prepared most conveniently by treating a carbonate with a strong acid,

$$Na_2^+CO_3^{=} + H_2^+SO_4^{=} \rightarrow H_2CO_3 + Na_2^+SO_4^{=}$$

and collecting (over water) the carbon dioxide resulting from the decomposition of the unstable carbonic acid.

$$H_2CO_3 \rightarrow H_2O + \overline{CO_2}$$

29.3. Properties of Carbon Dioxide

Carbon dioxide is a colorless, odorless gas, which does not support combustion and which is about 1.5 times as heavy as air. Under a pressure of 1 atm., the pure gas solidifies at $-78.47°C$. *At room temperature* and at atmospheric pressure carbon dioxide dissolves in water to the extent of about one volume of the gas to one volume of water. With increase in pressure, the solubility increases in accordance with Henry's law (Sec. 9.6) until a pressure of about 6 atm. is reached, after which the increase in solubility is less pronounced.

That carbon dioxide is an unusually stable compound is shown by the fact that it is not appreciably decomposed by heat except at very high temperatures. Above 2000°C., partial decomposition occurs in accordance with the equation,

$$2\overline{CO_2} \rightleftharpoons 2\overline{CO} + \overline{O_2}$$

Attention has already been called to the fact that carbon dioxide is reduced to the monoxide by reaction with hot carbon (Sec. 8.5). By reaction with water, carbon dioxide (carbonic anhydride) reacts *to a limited extent* to form carbonic acid,

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

in an equilibrium the forward reaction of which is favored by an increase in pressure and by the slight ionization of the resulting very weak electrolyte.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_i = 3 \times 10^{-7}$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{=} \qquad K_i = 6 \times 10^{-11}$$

29.4. Uses of Carbon Dioxide

Large quantities of carbon dioxide are consumed in the manufacture of carbonates of sodium by the Solvay process (Sec. 32.4) as well as in the production of other chemicals. A more familiar large-scale use for this simple compound is in the production of carbonated beverages. "Soda water" is produced by dissolving carbon dioxide in water containing suitable flavoring agents, by application of pressures of from 4 to 8 atm. (60 to 120 lb. per sq. in.). When the carbonated liquid is withdrawn into an open glass, the pressure is reduced to 1 atm, the solubility decreases, and the excess gas escapes and produces the effect of effervescence.

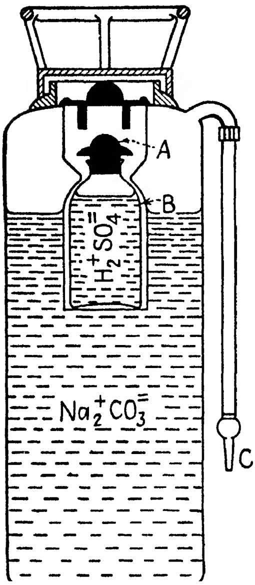


Fig. 127.—Fire extinguisher.

Fire Extinguishers. Because carbon dioxide does not support combustion, this gas finds extensive application in the manufacture of several different kinds of fire extinguishers. In the type shown in Fig. 127, inversion of the apparatus permits the stopper *A* to fall from the mouth of a bottle *B*, which contains sulfuric acid. This permits the acid to mix with the sodium carbonate (or sodium hydrogen carbonate) solution contained in the main vessel and to generate carbon dioxide gas.

$$Na_2^+CO_3^= + H_2^+SO_4^= \rightarrow Na_2^+SO_4^= + H_2O + \overline{CO_2}$$

Some of the gas dissolves in the aqueous solution, and the gas pressure developed within the apparatus forces the mixture out through the nozzle *C*, which is directed onto the flame. If some heavy molasses or similar gluelike material is added to the sodium carbonate solution and some aluminum sulfate is added to the sulfuric acid, the solution issues from the nozzle in the form of a foam in which the carbon dioxide gas is trapped. This heavy blanket of foam containing carbon dioxide settles over and around the burning object. The aluminum sulfate hydrolyzes to form aluminum hydroxide which, at the temperature of the flame, dehydrates to produce a crust of aluminum oxide over the flame. Both effects serve to extinguish the flame. The common Foamite fire extinguisher is an example of this type.

Dry Ice. If a commercial cylinder of liquid carbon dioxide is inverted and some of the liquid allowed to run out into a cloth bag or a special perforated metal container, only a part of the liquid will

evaporate. That which evaporates takes heat from the remainder and causes it to solidify in the form of a white solid resembling snow. This material, compressed into blocks, is sold commercially as *dry ice*. Since this solid vaporizes directly to a gas at $-78.47°C.$, evaporation produces no liquid residue. For this reason alone, the advantages of this *dry* refrigerant are obvious. The future will doubtless see a great expansion of the use of dry ice as a refrigerant.

When dry ice is mixed with a volatile liquid such as ether or acetone, a freezing mixture providing temperatures within the range of $-90°$ to $-100°C.$ (depending upon the pressure) results. Such freezing mixtures are commonly employed in scientific laboratory work where the maintenance of low temperatures is desired.

CARBIDES

Although the general term *carbide* applies to the binary compounds of the element carbon, this term is used in systematic nomenclature only when carbon is the more electronegative of the two elements involved. Thus, CO_2 is called *carbon dioxide* and not oxygen carbide since oxygen is more electronegative than carbon. Although carbon forms binary compounds with most of the nonmetals, metalloids, and metals, only a few of the more common members of this class will be considered here.

29.5. Carbon Disulfide

Carbon disulfide (CS_2) is produced commercially by the direct union of sulfur vapor and hot carbon at considerably elevated temperatures in a furnace of the type shown in Fig. 128. The reaction must be carried out in the absence of air. Solid sulfur and carbon (usually in the form of coke) are fed continuously into the furnace which is heated electrically to a temperature sufficient to vaporize the sulfur and to maintain the carbon at a temperature such that combination will occur when the sulfur vapor comes into contact with the solid carbon. Since carbon disulfide is a low-boiling liquid (46°C.), it passes out of the furnace from which the vapors are conducted into a condenser. Although the resulting pale-yellow liquid may be purified by distillation, the crude product is used directly for many purposes.

The yellow color of commercial carbon disulfide is due to the presence of small amounts of dissolved sulfur. The rather disagreeable odor of this material is also due to the presence of impurities. Carbon disulfide is a highly flammable liquid which is very poisonous and which is only very slightly soluble in water.

The large-scale uses of carbon disulfide center largely about its

properties as a solvent. Many fats, oils, waxes, and resins are abundantly soluble in this liquid. Despite the disadvantages attendant upon its volatility, flammability, and toxicity, carbon disulfide is used extensively as a solvent and in processes for the manufacture of rubber products, lacquers, varnishes, cellophane, etc. Because of its toxicity, this compound is used to some extent as an insecticide and as a poison for rodents.

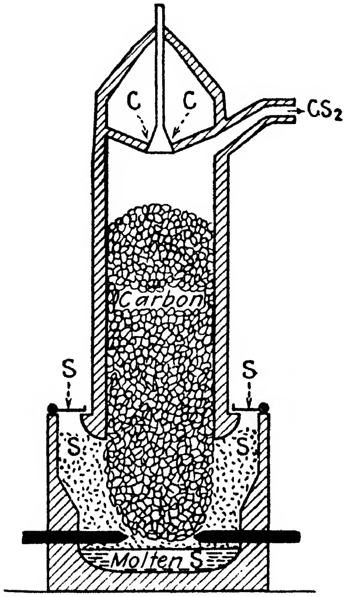


FIG. 128.—Electric furnace for the production of carbon disulfide.

29.6. Silicon Carbide

Silicon carbide (SiC) more familiarly known by the trade name *Carborundum*, is produced by heating a mixture of coke, sawdust, sand, and salt to about 3000°C. in an electric furnace (Fig. 129).

$$SiO_2 + 3C \rightarrow SiC + 2\overline{CO}$$

The salt is added to the charge placed in the furnace in order to render the charge a better conductor and to permit the partial removal of any iron present. This latter is accomplished owing to the formation of iron chloride which is volatile at the temperature of the furnace. The sawdust renders the entire charge more porous and thus facilitates the escape of volatile products. Because the charge as a whole is not a particularly good conductor, a core of pure carbon is placed in the center of the charge. When the heated charge is cooled, a mass of crystals of silicon carbide forms in the region of the carbon core.

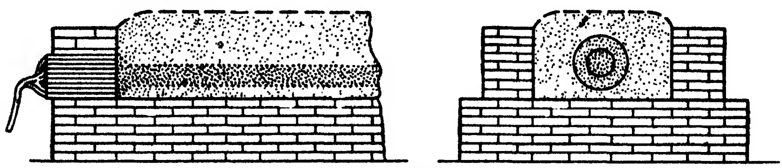


FIG. 129.—Electric furnace for the production of silicon carbide.

The product thus obtained consists of sharp iridescent crystals which are extremely inactive chemically. The most notable property of this material, however, is its hardness. Carborundum is almost as hard as diamond and is used in general as an *abrasive*, *i.e.*, in the manu-

facture of grinding stones and wheels, polishing papers and cloths, etc. A lesser use lies in the incorporation of coarse Carborundum crystals into concrete or terrazzo floors to render them slipproof.

29.7. Calcium Carbide

The calcium compound having the formula CaC_2 is that which is implied when the common term *carbide* is used. That is, just as the term *salt* commonly denotes sodium chloride, so the term *carbide* is applied to calcium carbide. This compound is formed commercially by the reaction between quicklime and coke in an electric furnace at 2800° to 2900°C.

$$CaO + 3C \rightarrow CaC_2 + \overline{CO}$$

The equipment is designed so as to permit continuous and automatic operation, and the resultant molten calcium carbide is withdrawn from the furnace and allowed to cool, whereupon it solidifies to a dense gray solid.

Calcium carbide is an important chemical in the manufacture of acetylene (Sec. 33.8),

$$CaC_2 + 2H_2O \rightarrow \overline{C_2H_2} + \underline{Ca^{++}(OH)_2^-}$$

and in the manufacture of calcium cyanamide (Sec. 29.10),

$$CaC_2 + \overline{N_2} \rightarrow CaNCN$$

which, in turn, is used in the production of ammonia, sodium cyanide, etc.

OXIDES OF SILICON

The nonmetal silicon forms two oxides, SiO and SiO_2. The monoxide is relatively unimportant while silicon dioxide is a compound of major value in many chemical processes and products.

29.8. Silicon Monoxide

When silicon dioxide is reduced by carbon at high temperatures, silicon monoxide is formed.

$$SiO_2 + C \rightarrow SiO + \overline{CO}$$

Silicon monoxide is a light-brown solid which finds limited use as a pigment.

29.9. Silicon Dioxide

Because silicon dioxide is so readily available in nature, there is only infrequent need to produce this compound in either the laboratory or

the plant. Many familiar materials consist of silicon dioxide (or *silica*) in varying degrees of purity. Thus, flint, agate, amethyst, quartz, onyx, opal, granite, petrified wood, sand, sandstone, etc., are all materials that consist entirely or largely of silica. The student will recognize that all these materials have a variety of common uses and will recall, from preceding discussions, cases in which silicon dioxide is used in certain commercial chemical processes.

One of the most significant properties of silica is its resistance to chemical attack. This compound is insoluble in water and is unreactive toward all acids except hydrofluoric with which the following reaction occurs:

$$SiO_2 + 4H^+F^- \rightarrow \overline{SiF_4} + 2H_2O$$

With strong bases such as sodium hydroxide, silica reacts to form *silicates.*

$$SiO_2 + 2Na^+OH^- \rightarrow Na_2^+SiO_3^= + H_2O$$

from which it is seen that SiO_2 is the anhydride of silicic acid (H_2SiO_3). When silica is fused with dry sodium carbonate, sodium sulfate, or any salt formed from an acid having a volatile anhydride, the latter is released and silicates are produced.

$$Na_2^+CO_3^= + SiO_2 \rightarrow Na_2^+SiO_3^= + \overline{CO_2}$$
$$Na_2^+SO_4^= + SiO_2 \rightarrow Na_2^+SiO_3^= + \overline{SO_3}$$

Finally, attention should be called to the marked contrast between the properties (both chemical and physical) of the related compounds, CO_2 and SiO_2.

AMMONIA

Of the simple hydrogen compounds of the elements, only water is more widely useful than ammonia. In the gaseous and liquid states, and in solutions, ammonia serves a variety of needs in the chemical laboratory, the home, and the industries.

29.10. Production of Ammonia

For small-scale laboratory use, ammonia may be prepared by any of the following methods.

1. *Treatment of an Ammonium Salt with a Strong Base.* This is perhaps the best available laboratory method and is illustrated by the following equations:

$$(NH_4)_2^+SO_4^= + 2Na^+OH^- \rightarrow Na_2^+SO_4^= + 2\overline{NH_3} + 2H_2O$$
$$2NH_4^+Cl^- + Ca^{++}(OH)_2^- \rightarrow Ca^{++}Cl_2^- + 2\overline{NH_3} + 2H_2O$$

2. *Dissociation of an Ammonium Salt.* Gaseous ammonia is liberated by heating the normal ammonium salt of a (relatively) nonvolatile acid, *e.g.*,

$$(NH_4)_2^+SO_4^= + \text{heat} \rightarrow NH_4^+HSO_4^- + \overline{NH_3}$$

Ammonium phosphate would serve equally well. If, however, one used the ammonium salt of a volatile acid such as hydrochloric,

$$NH_4^+Cl^- + \text{heat} \rightarrow \overline{NH_3} + \overline{HCl}$$

ammonia would be liberated together with hydrogen chloride gas and the two gases would recombine to form the original salt, ammonium chloride.

3. *Hydrolysis of the Nitride of a Metal.* The nitrides of metals such as magnesium react with water to produce ammonia and the hydroxide of the metal; thus,

$$Mg_3N_2 + 6HOH \rightarrow 3Mg(OH)_2 + 2\overline{NH_3}$$

4. *Volatilization of Ammonia from Aqueous Solutions.* When an aqueous solution of ammonia (ammonium hydroxide) is warmed, some of the dissolved ammonia volatilizes in the gaseous form. This result is to be anticipated in the light of the manner in which the solubility of gases in liquids is generally influenced by an increase in temperature (Sec. 9.6). In the use of this method, the quantity of heat supplied should be such that a minimum quantity of water will be vaporized.

None of the preceding methods would be suitable for industrial use. For many years the bulk of the ammonia produced commercially was obtained as a by-product of the destructive distillation of coal (Sec. 35.3). More recently, however, there have been devised processes that are far more satisfactory.

Haber Process. This method, which is sometimes called the *synthetic ammonia process*, is based upon the following reactions:

$$\overline{N_2} + 3\overline{H_2} \rightleftharpoons 2\overline{NH_3} + 24{,}400 \text{ cal.}$$

The manner in which this equilibrium is influenced by changes in temperature and pressure has been discussed in Chap. XII and should be reviewed by the student. In practice, ammonia is produced by the Haber process at temperatures ranging from 400° to 600° and at pressures between 200 and 1000 atm. Catalysts that are suitable for use in this process include a mixture of the oxides of iron, potassium, and aluminum; iron oxide alone; mixtures of iron and molybdenum; the metals platinum, osmium, uranium; and a number of others as well.

Cyanamide Process. Although this process employs relatively inexpensive raw materials, it cannot compete under normal conditions with the Haber process. Formation of ammonia by the cyanamide process is based upon the reaction between calcium cyanamide and steam,

$$CaNCN + 2H_2O \rightarrow CaCO_3 + 2NH_3$$

One of the chief disadvantages involved in this process is the large quantity of energy that must be employed in the production of calcium carbide and in its conversion to calcium cyanamide.

29.11. Uses of Ammonia

The various uses of ammonia may be concerned with the use of the compound as such or in the form of compounds made from ammonia. In the liquid state, much ammonia is used as the refrigerant liquid in commercial refrigeration plants and in the manufacture of ice. Some liquid ammonia is used both in the laboratory and commercially as a solvent, and its solvent properties are in many respects similar to those of water. Great quantities of ammonia are used in the manufacture of nitric acid (Sec. 31.3), sodium hydrogen carbonate and normal sodium carbonate (Sec. 32.4), aqueous ammonia (or ammonium hydroxide), ammonium salts for use as fertilizers, and many other useful chemicals.

OXIDES OF NITROGEN AND PHOSPHORUS

The generally abnormal character of an "introductory element" is well illustrated by the case of nitrogen. With respect to oxide formation, for example, this element exhibits more diversity than any other element in Group V of the periodic arrangement.

29.12. The Common Oxides of Nitrogen and Phosphorus

The related elements nitrogen and phosphorus combine with oxygen to form those oxides which are to be expected on the basis of the position of these elements in the periodic table. In addition, nitrogen forms several other oxides (Sec. 24.4). Although each of these compounds has its own specific uses or participates in certain reactions that render these oxides of scientific interest, the chief relationship that it is wished to portray here is that between these oxides (acid anhydrides) and the corresponding acids. This information is incorporated in Table 39.

TABLE 39

OXIDES OF NITROGEN AND PHOSPHORUS

Oxide		Related acid	
Formula	Name	Formula	Name
N_2O	Nitrous oxide*		
NO	Nitric oxide		
N_2O_3	Nitrogen trioxide	HNO_2	Nitrous acid
NO_2	Nitrogen dioxide		
N_2O_5	Nitrogen pentoxide	HNO_3	Nitric acid
P_2O_3	Phosphorus trioxide	H_3PO_3	Phosphorus acid
P_2O_5	Phosphorus pentoxide	H_3PO_4	Phosphoric acid

* Laughing gas.

Nitrogen dioxide may be looked upon as being, at the same time, the anhydride of both nitrous and nitric acids. This view is based upon the fact that nitrogen dioxide reacts with *cold* water as follows:

$$2\overline{NO_2} + H_2O \rightarrow HNO_2 + HNO_3$$

If, however, hot water is used, the reaction is

$$3\overline{NO_2} + H_2O \rightarrow 2HNO_3 + \overline{NO}$$

The two oxides of phosphorus are, in fact, dimeric and their formulas accordingly may be written more properly as P_4O_6 and P_4O_{10}.

OXIDES OF SULFUR

Of the two common oxides of sulfur, the dioxide is by far the more important. Sulfur trioxide (SO_3), the anhydride of sulfuric acid, is a strong oxidizing agent which finds limited uses other than in the manufacture of H_2SO_4. Solutions of sulfur trioxide in concentrated sulfuric acid are known as *fuming sulfuric acid* or *oleum*, and such solutions are useful in the laboratory and in a few commercial processes.

29.13. Sulfur Dioxide

The best laboratory method for the preparation of sulfur dioxide (SO_2) is based upon the metathetical reaction between a sulfite and a strong acid, *e.g.*,

$$Na^+HSO_3^- + H_2^+SO_4^= \rightarrow Na^+HSO_4^- + H_2O + \overline{SO_2}$$

or

$$Na_2^+SO_3^= + H_2^+SO_4^= \rightarrow Na_2^+SO_4^= + H_2O + \overline{SO_2}$$

Less convenient but otherwise equally satisfactory is the preparation involving the reduction of *hot* concentrated sulfuric acid by means of

copper, carbon, or sulfur. The oxidation-reduction reaction involved may be illustrated by the following equations:

$$\begin{array}{ll}
(a) & Cu^0 - 2e^- \rightarrow Cu^{++} \\
(b) & \overset{VI+}{S} + 2e^- \rightarrow \overset{IV+}{S} \\
\hline
(c) & Cu^0 + \overset{VI+}{S} \rightarrow Cu^{++} + \overset{IV+}{S} \\
(d) & Cu^0 + H_2SO_4 + H_2^+SO_4^{=} \rightarrow Cu^{++}SO_4^{=}\,\overline{SO}_2 + 2H_2O
\end{array}$$

If sulfur is employed as the reducing agent, the equations are as follows:

$$\begin{array}{ll}
(a) & S^0 - 4e^- \rightarrow \overset{IV+}{S} \\
(b) & 2\overset{VI+}{S} + 4e^- \rightarrow 2\overset{IV+}{S} \\
\hline
(c) & S^0 + 2\overset{VI+}{S} \rightarrow 3\overset{IV+}{S} \\
(d) & S^0 + 2H_2SO_4 \rightarrow 3\overline{SO}_2 + 2H_2O
\end{array}$$

Commercially, sulfur dioxide is produced (*a*) by the roasting of sulfides, *e.g.*,

$$\begin{array}{c}
2PbS + 3\overline{O}_2 \rightarrow 2PbO + 2\overline{SO}_2 \\
4FeS_2 + 11\overline{O}_2 \rightarrow {}_3\,2Fe_2O + 8\overline{SO}_2
\end{array}$$

or (*b*) by the direct union of elememtal sulfur and oxygen.

$$S + \overline{O}_2 \rightarrow \overline{SO}_2$$

Pure sulfur dioxide is a colorless gas which has an irritating odor and which is soluble in water. The gas may be liquefied readily and is usually stored and transported in the liquid state in steel cylinders. This substance is a strong reducing agent, and therefore a poor oxidizing agent.

The chief uses of sulfur dioxide are concerned with (*a*) the hydration of SO_2 to form sulfurous acid which, in turn, is used to produce sulfites, notably $Ca(HSO_3)_2$, which is used in large quantities in the pulp and paper industries; (*b*) the oxidation of SO_2 to SO_3 which is then converted to sulfuric acid; (*c*) the bleaching of silk, straw, wool, and other fabrics. This use depends upon the fact that sulfur dioxide forms unstable colorless compounds with the colored pigments in these fibers. Because of the relative instability of these colorless compounds, the bleaching action of sulfur dioxide is seldom permanent; (*d*) the removal of excess chlorine or hypochlorous acid from fabrics which have been bleached with chlorine,

$$HClO + \overline{SO}_2 + H_2O \rightarrow H^+Cl^- + H_2^+SO_4^{=}$$

(*e*) the refrigeration units in which liquid sulfur dioxide is used as the refrigerant liquid.

EXERCISES

1. Write equations representing laboratory methods for the preparation of the following compounds: (*a*) carbon dioxide, (*b*) sulfur dioxide, (*c*) ammonia, (*d*) carbon monoxide, (*e*) sulfur dioxide.

2. Explain briefly the manner in which (*a*) sulfur dioxide acts as a bleaching agent and (*b*) carbon monoxide poisoning is produced.

3. Make a detailed comparison of the physical and chemical properties of silicon dioxide and carbon dioxide.

4. List the raw materials needed for the commercial production of Carborundum. Cite the reason for the use of each, and write the equation for the principal reaction involved.

5. What volume of acetylene gas, at 25°C. and 710 mm., can be produced from 1 lb. of pure calcium carbide?

6. Write equations for the reactions that occur in the commercial processes by means of which the following compounds are produced: (*a*) sulfur dioxide, (*b*) calcium carbide, (*c*) carbon dioxide, (*d*) calcium cyanamide.

7. List important large-scale uses for (*a*) ammonia, (*b*) sulfur dioxide, (*c*) carbon dioxide, (*d*) Carborundum, (*e*) calcium carbide, (*f*) carbon disulfide, (*g*) silicon dioxide.

8. What are the essential features of the ordinary Foamite fire extinguisher?

9. In the commercial production of carbon disulfide, why must the reaction be carried out in the absence of air?

10. By means of equations, summarize the chemical reactions in which silicon dioxide participates.

11. What industries would be expected to produce sulfur dioxide as a by-product?

12. Why is the Haber process not suitable for the preparation of small quantities of ammonia for use in the laboratory?

13. What factors would have a bearing upon the choice of location for a plant designed to produce ammonia by the Haber process?

14. Assuming that the nomenclature is to be entirely systematic, suggest names for the compounds H_2O and NH_3.

SUGGESTED READING

Journal of Chemical Education

QUINN, Carbon Dioxide, **7**, 151, 403, 637 (1930).

KILLEFFER, The Industry of Solid Carbon Dioxide, **19**, 482 (1942).

KOBE, The Other Oxides of Carbon, **8**, 232 (1931).

SCHEFLAN, Extinguishing Fires with Chemicals, **9**, 1503 (1932).

KOBE, The Sulfides of Carbon, **8**, 867 (1931).

COOPER, Modern Abrasives, **19**, 122 (1942).

LARSON, Synthetic Ammonia by Catalysis, **3**, 284 (1926).

CURTIS, Ammonia, **19**, 188 (1942).

EMMETT, Studies on the Mechanism of Ammonia Synthesis over Iron Catalysts, **7**, 2571 (1930).

Industrial and Engineering Chemistry

JOHNSTONE, Sulfur Dioxide, **34**, 1017 (1942).

CHAPTER XXX

HALOGENS AND COMPOUNDS OF THE HALOGENS

The elements of the main family of periodic Group VII have already been considered from the standpoint of their interrelationships (Sec. 13.5). These similarities and differences are equally impressive if one considers not only the elements as such but their compounds as well.

30.1. Occurrence of the Halogens

All the elements of the halogen family occur in nature in the form of their compounds but, because of their marked chemical activity, they are never found in nature in the uncombined state.

In compound form, *fluorine* is a fairly abundant element which constitutes approximately 0.1 per cent of the solid crust of the earth. The chief fluorine-bearing minerals are *fluorspar* (CaF_2), *cryolite* (Na_3AlF_6), and *fluorapatite* [$CaF_2[Ca_3(PO_4)_2]_3$].

Ordinary rock salt (sodium chloride) is the chief commercial source of *chlorine*. In the United States, the salt wells in Michigan and the salt mines of Texas and Louisiana are rich sources of this material. Chlorine is also obtained from the minerals *carnallite* ($MgCl_2 \cdot KCl \cdot 3H_2O$) and *kainite* ($MgSO_4 \cdot KCl \cdot 6H_2O$). Salt deposits containing combined chlorine are widely scattered over all parts of the world and are among the most abundant, cheap, and useful raw materials of the chemical industries. Oceanic waters have a high salt content, and the waters of salt lakes such as the Great Salt Lake in Utah contain approximately 20 per cent of sodium chloride.

Although less abundant than chlorine, the occurrence of *bromine* parallels that of chlorine. Thus, bromine is found in salt deposits in the form of the bromides of sodium, potassium, magnesium, etc., and in sea water. Although in this country much bromine is produced from the salt wells in Michigan, the production of bromine from sea water in recent years has become the most important source of this element. *Iodine* also occurs in sea water and in numerous seaweeds including kelp, from which iodine has been extracted on a commercial scale. The greater part of the iodine of commerce is obtained from sodium iodate ($NaIO_3$) and sodium periodate ($NaIO_4$), both of which are associated with the enormous deposits of sodium nitrate in Chile.

Both chlorine and iodine are found in, and are essential to, the human body. The gastric juices normally contain from 0.25 to 0.4 per cent of hydrochloric acid, while the chloride ion concentration of the blood is approximately 0.25 per cent. Iodine occurs in the thyroid gland in the form of a complex organic compound which is essential to the proper functioning of this gland. Iodine deficiency in the human body is largely responsible for the development of goiter and cretinism. For this reason, iodine, frequently in the form of sodium iodide added to table salt (*i.e.*, iodized salt), is added to the diet as a preventive. In the United States, waters in the coastal regions contain adequate supplies of iodine, while in the inland states, iodine deficiency is much more prevalent.

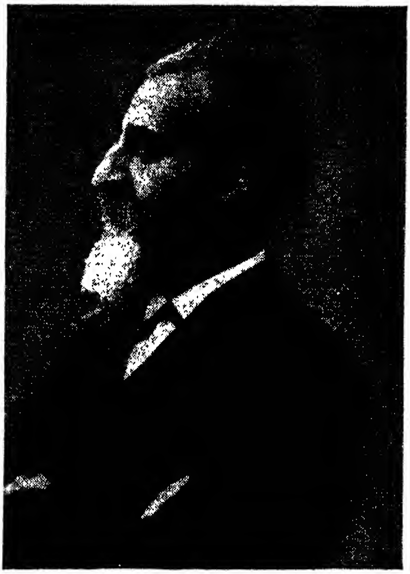


Fig. 130.—Henri Moissan (1852–1906).

30.2. Methods of Preparation

A study of the means whereby the elements of the halogen family may be prepared either in the laboratory or on an industrial scale not only serves to bring some new and worth-while facts before the student but also provides further insight into the interrelationships of these elements.

Fluorine. The distinguished French chemist, Moissan (Fig. 130), first prepared fluorine by the electrolysis of a solution of potassium fluoride in liquid hydrogen fluoride. Because of the extreme chemical activity of this element, the electrolytic cell employed had to be made of platinum. At the present time, fluorine is produced in the laboratory and commercially by the electrolysis of fused potassium hydrogen fluoride (KHF_2) in the manner already described (Sec. 22.4).

Chlorine. The preparation of chlorine in the laboratory is accomplished best by the oxidation of hydrogen chloride using any of a wide variety of oxidizing agents, *e.g.*, HNO_3, $KMnO_4$, $K_2Cr_2O_7$, MnO_2, $KClO_3$, etc. The HCl may be used in the form of concentrated hydrochloric acid or may be prepared by the reaction between sodium chloride and concentrated sulfuric acid.[1] The over-all reactions are

[1] This procedure is made possible by the fact that concentrated sulfuric acid is

illustrated by the following equations:

$$K^+ClO_3^- + 6H^+Cl^- \rightarrow K^+Cl^- + 3H_2O + 3\overline{Cl}_2^0$$
$$2K^+MnO_4^- + 16H^+Cl^- \rightarrow 2Mn^{++}Cl_2^- + 2K^+Cl^- + 8H_2O + 5\overline{Cl}_2^0$$
$$MnO_2 + 4H^+Cl^- \rightarrow Mn^{++}Cl_2^- + 2H_2O + \overline{Cl}_2^0$$

Or, in case the HCl is produced as needed,

$$Na^+Cl^- + H_2SO_4 \rightarrow \overline{HCl} + Na^+HSO_4^-$$
$$Na^+Cl^- + Na^+HSO_4^- \rightarrow \overline{HCl} + Na_2^+SO_4^=$$

The oxidation of hydrogen chloride by atmospheric oxygen,

$$4\overline{HCl} + \overline{O}_2^0 \rightarrow 2\overline{Cl}_2^0 + 2\overline{H_2O}$$

at elevated temperatures and in the presence of suitable catalysts, was once used as a commercial procedure for the production of chlorine. However, this process cannot now be operated economically in competition with methods involving electrolysis. As has been described previously (Secs. 22.4 and 22.5), chlorine is now produced commercially almost exclusively by the electrolysis of aqueous solutions of chlorides or of fused chlorides.

Bromine. The laboratory preparation of bromine may be accomplished in a manner analogous to that described for chlorine. Thus, treatment of a bromide with a mixture of sulfuric acid and manganese dioxide results in the liberation of elemental bromine.

$$2Na^+Br^- + 2H_2^+SO_4^= + MnO_2 \rightarrow Mn^{++}SO_4^= + Na_2^+SO_4^= + 2H_2O + \overline{Br}_2^0$$

Although this equation accounts for the liberation of bromine, this product also arises by virtue of the occurrence of another reaction. Although not a sufficiently strong oxidizing agent to liberate chlorine from hydrogen chloride, concentrated sulfuric acid does act upon hydrogen bromide with a resultant *partial* oxidation to bromine.

$$2HBr + H_2SO_4 \rightarrow \overline{Br}_2^0 + \overline{SO_2} + 2H_2O$$

Hence, when one treats sodium bromide with concentrated sulfuric acid and manganese dioxide, the hydrogen bromide liberated by the initial reaction,

$$2Na^+Br^- + H_2^+SO_4^= \rightarrow 2\overline{HBr} + Na_2^+SO_4^=$$

may be oxidized to bromine either by the concentrated H_2SO_4 or by the MnO_2.

not a sufficiently strong oxidizing agent to oxidize HCl. Hence, a stronger oxidizing agent must be used to produce Cl_2^0 from the HCl liberated in the reaction between NaCl and H_2SO_4.

The commercial production of bromine from salt-well brines or from sea water (Fig. 131) depends upon the fact that chlorine is capable of displacing bromine from its salts (Sec. 13.5). Bromine is extracted from sea water by a process involving the following steps:

1. Sea water is rendered slightly acidic by the addition of sulfuric acid, after which the water solution is sprayed into towers containing

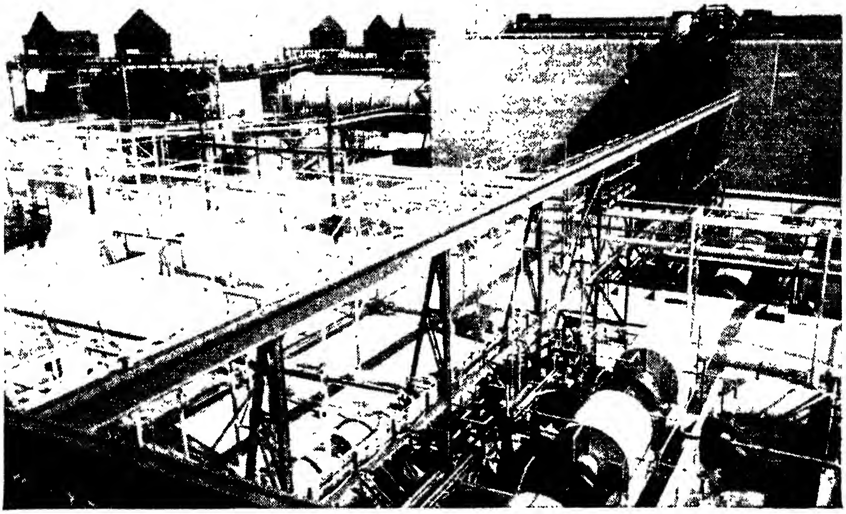


Fig. 131.—View of a plant engaged in the extraction of bromine from sea water at Freeport, Texas. (*Courtesy of The Dow Chemical Company, Texas Division.*)

gaseous chlorine. If M is used to represent a metal that forms a soluble bromide, the reaction may be represented as follows:

$$2M^+Br^- + \overline{Cl_2^0} \rightarrow 2M^+Cl^- + \overline{Br_2^0}$$

2. The liberated bromine is carried from the tower by means of a stream of air and into an absorber containing sodium carbonate solution. By reaction with sodium carbonate, the bromine is converted to sodium bromide and sodium bromate.

$$3Na_2^+CO_3^= + 3Br_2^0 \rightarrow 5Na^+Br^- + Na^+BrO_3^- + 3\overline{CO_2}$$

3. When bromine is needed, this solution is acidified with sulfuric acid, whereupon hydrobromic and bromic acids are formed.

$$5Na^+Br^- + Na^+BrO_3^- + 3H_2^+SO_4^= \rightarrow 3Na_2^+SO_4^= + 5H^+Br^- + H^+BrO_3^-$$

Owing to the oxidizing action of bromic acid, bromine is liberated in accordance with the following equation:

$$5H^+Br^- + H^+BrO_3^- \rightarrow 3Br_2^0 + 3H_2O$$

4. The resulting bromine may be removed in a current of steam and subsequently separated from the water by condensation or may be used directly in the manufacture of ethylene dibromide.

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

Although sea water contains only 67 parts of bromine in 1,000,000 parts of solution, this seemingly rather involved process is both efficient and economical. One cubic mile of sea water contains approximately 300,000 tons of bromine, and the process described above permits the recovery of about 80 per cent of the available bromine.

Iodine. Because of the close chemical similarity between chlorine, bromine, and iodine, it is to be anticipated that iodine might be prepared in a manner analogous to that used in the preparation of bromine. Such is the case. In the laboratory, iodine is most conveniently produced by treating an iodide with sulfuric acid and manganese dioxide. Just as in the case of bromine, the initial reaction is that between the iodide and sulfuric acid.

$$Na^+I^- + H_2^+SO_4^= \rightarrow H^+I^- + Na^+HSO_4^-$$
$$Na^+I^- + Na^+HSO_4^- \rightarrow H^+I^- + Na_2^+SO_4^=$$

The hydrogen iodide is oxidized by either or both of the oxidizing agents present, *i.e.*, concentrated H_2SO_4 or MnO_2,

$$4H^+I^- + MnO_2 \rightarrow Mn^{++}I_2^- + \underline{I_2^0} + 2H_2O$$

or

$$2H^+I^- + H_2SO_4 \rightarrow \underline{I_2^0} + \overline{SO_2} + 2H_2O$$

In addition to relatively small amounts of iodine that are extracted from the ashes of kelp, the great bulk of iodine produced commercially is obtained from sodium iodate. This compound occurs along with sodium nitrate (Chile saltpeter), and the iodine is extracted by treating the iodate with sodium hydrogen sulfite.

$$2Na^+IO_3^- + 5Na^+HSO_3^- \rightarrow \underline{I_2^0} + 2Na_2^+SO_4^= + 3Na^+HSO_4^- + H_2O$$

The resulting solution is evaporated to dryness and heated further, whereupon the iodine sublimes and thus may be separated from the other products of the reaction.

30.3. Uses of the Halogens

Owing to the extreme chemical activity of *fluorine*, the chief uses of this element arise in connection with the production of compounds of

fluorine. Thus, sodium fluoride is commonly used as a flux, as an insecticide, and as a wood preservative. Ammonium fluoride is sometimes used as a disinfectant. The compound dichlorodifluoromethane (CCl_2F_2) is used as an insecticide propellent and is an important commercial refrigerant (Freon) particularly well suited for use in domestic refrigeration units.

Of the elements of the halogen family, *chlorine* is by far the most useful. This fact becomes evident when one learns that the annual production of chlorine in the United States alone amounts to approximately ¼ million tons. Much of this chlorine is used in the bleaching of fabrics, wood pulp, etc. Considerable quantities of this element are used in treating water supplies for the purpose of destroying harmful bacteria. Many of the poisonous gases used in warfare were compounds of chlorine. Thus, this element has been used extensively in the production of mustard gas [$(ClC_2H_4)_2S$], chloropicrin (CCl_3NO_2), phosgene ($COCl_2$), etc. Other important and large-scale uses of chlorine are found in the manufacture of compounds such as chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), bleaching powder ($CaOCl_2$), and a host of other compounds that are useful in the home, the industries, and the laboratory.

That *bromine* is relatively a less important element from the standpoint of its applications may be seen from the fact that the annual production of bromine in this country is only about one-twentieth as great as that of chlorine. At the present time, the chief use of bromine is in the manufacture of ethylene dibromide ($C_2H_4Br_2$) which is used in the production of high-test gasolines. Bromine is used also in the production of other bromine compounds. Thus, potassium bromide is used medicinally as a sedative, silver bromide is used in photographic processes, while other compounds of bromine are used in the production of dyes.

Undoubtedly the most familiar use of *iodine* is in tincture of iodine which is so commonly used as an antiseptic. This consists of a solution of iodine and potassium iodide in alcohol and is one of the most effective antiseptics known. Iodine is used to make many useful compounds including sodium and potassium iodides which are important laboratory reagents, silver iodide which (like silver bromide) is used in photography, and numerous organic compounds of iodine which are useful in drugs, in the production of dyes, etc.

30.4. Hydrogen Compounds of the Halogens

Each member of the halogen family combines with hydrogen to form a compound of the type HX, where X represents a halogen.

The hydrogen compound of fluorine is exceptional in that it exists in different molecular forms from HF to H_6F_6. For the sake of simplicity, the formula HF will be employed consistently.

General Methods of Preparation. There are two general methods which, with appropriate modifications, may be used to produce the hydrogen compounds of the halogens.

1. *Direct Union of the Elements.* The manner in which the halogens react with hydrogen demonstrates admirably the trend in chemical activity within this group of elements. Fluorine and hydrogen combine with explosive violence even in the absence of light and at low temperatures. Chlorine and hydrogen do not react readily in the dark at ordinary temperatures, but under the influence of the actinic rays of a bright light (or sunlight) their union is violent. Bromine and hydrogen combine only upon application of heat while iodine and hydrogen combine only upon elevation of the temperature in the presence of a catalyst such as spongy platinum. The following thermochemical equations show the quantities of heat involved and provide evidence of the marked decrease in chemical activity of the halogens with increasing atomic number:

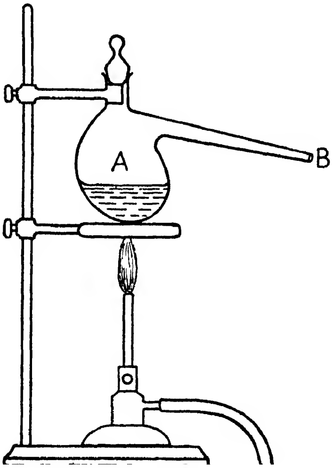


FIG. 132.—Apparatus for preparation of hydrogen compounds of the halogens.

$$H_2 + F_2 \rightarrow 2HF + 128{,}000 \text{ cal.}$$
$$H_2 + Cl_2 \rightarrow 2HCl + 44.120 \text{ cal.}$$
$$H_2 + Br_2 \rightarrow 2HBr + 17{,}300 \text{ cal.}$$
$$H_2 + I_2 \rightarrow 2HI - 11{,}820 \text{ cal.}$$

For practical purposes, only hydrogen chloride is produced in any appreciable quantity by direct union.

2. *Treatment of a Salt with a Strong Acid.* The metathetical reaction between a salt and a strong acid may be used in the preparation of compounds of the type HX, provided the correct reactants are chosen. Almost any salt containing the desired halogen may be employed, but one would, of course, select a cheap and readily available salt. The acid selected must be *concentrated*, *nonvolatile*, and *nonoxidizing*. The reasons for these requirements will become evident from a con-

sideration of a specific case. If, as would be convenient in the laboratory, an apparatus of the type shown in Fig. 132 were employed, the HX would be formed in the reaction mixture in the retort A. If this reaction mixture contained water (*i.e.*, if the acid were not concentrated), the HX would dissolve in the water and hence would not escape at B as desired. If a volatile acid were used, some of this acid would escape at B along with the HX, and hence the material collected would be a mixture and not the anticipated pure HX. Finally, if there is employed an acid which acts as an oxidizing agent toward the desired HX, one would obtain again not a pure HX but a mixture of HX and the elemental halogen X_2.

For the preparation of hydrogen fluoride and hydrogen chloride, the following equations represent the use of suitable reactants:

$$Ca^{++}F_2^- + H_2^+SO_4^= \rightarrow \underline{CaSO_4} + 2\overline{HF}$$

and

$$Na^+Cl^- + H_2^+SO_4^= \rightarrow Na^+HSO_4^- + \overline{HCl}$$
$$Na^+Cl^- + Na^+HSO_4^- \rightarrow Na_2^+SO_4^= + \overline{HCl}$$

Concentrated sulfuric acid is relatively *nonvolatile* and does not act as an oxidizing agent toward HF and HCl. However, as has already been pointed out (Sec. 30.2), both HBr and HI are oxidized to the respective halogens by concentrated sulfuric acid. Consequently, to prepare pure hydrogen bromide or pure hydrogen iodide, one would use sodium bromide or sodium iodide in reaction with concentrated phosphoric acid which is also relatively nonvolatile and which does not act as an oxidizing agent toward either HBr or HI.

Other Methods of Preparation. For each of the hydrogen compounds of the halogens there are certain specific methods that may be used to advantage in the laboratory. Thus, hydrogen fluoride may be produced by the heating of potassium hydrogen fluoride

$$KHF_2 + \text{heat} \rightarrow KF + \overline{HF}$$

Hydrogen bromide and hydrogen iodide may be prepared readily by the hydrolysis of phosphorus tribromide and phosphorus triiodide, respectively.

$$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3\overline{HBr}$$
$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3\overline{HI}$$

Properties. All four of the hydrogen halides are colorless gases with pungent, irritating odors. Certain physical properties of these compounds have already been tabulated elsewhere. These compounds in the pure dry condition are predominantly covalent. However, when they are dissolved in water, all except hydrogen fluoride

form solutions (by reaction)

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

which behave as very strong acids. With increase in atomic number of the halogen, the hydrogen halides become increasingly unstable and become increasingly strong reducing agents (hence, increasingly weak oxidizing agents).

Although hydrofluoric acid is a relatively weak acid, it is unusually reactive in certain other respects. For example, it has an extremely corrosive action on the skin and thereby produces burns which are very painful and slow to heal. Hydrofluoric acid also attacks the silica and silicates present in glass.

$$SiO_2 + 4H^+F^- \rightarrow \overline{SiF_4} + 2H_2O$$
$$CaSiO_3 + 6H^+F^- \rightarrow \overline{SiF_4} + Ca^{++}F_2^- + 3H_2O$$

These and similar reactions are involved in the *etching of glass*. In recent years, hydrogen fluoride has come into use as a catalyst in the production of aviation gasoline.

30.5. Oxygen Compounds of the Halogens

The regularities exhibited by the halogens in their combinations with hydrogen having been noted, it becomes of interest to study the compounds formed by the halogens and oxygen. A list of the known oxides is given in Table 40.

TABLE 40

OXIDES OF THE HALOGENS

Halogen	Formulas of Known Oxides
F	F_2O, F_2O_2
Cl	Cl_2O, ClO_2, ClO_3 (or Cl_2O_6), Cl_2O_7, ClO_4(?)
Br	Br_2O, BrO_2, Br_3O_8
I	I_2O_4, I_2O_5, IO_4(?), I_4O_9

Most of these oxides are unstable and, even at ordinary temperatures, some of them decompose with explosive violence. For the most part, they are very strong oxidizing agents. Of the four halogens, fluorine and bromine show but little tendency to combine with oxygen; in fact, all the known oxides of these elements have been discovered since about 1930.

30.6. Ternary Oxygen Acids of the Halogens

Just as the halogens differ with respect to their tendencies toward combination with oxygen and the stability of the resulting oxide, so these elements differ appreciably in regard to the properties of their

ternary oxygen acids. In Table 41 there are listed the names and formulas of the known acids, together with the names and formulas of the corresponding sodium salts. An inspection of this table will make evident the manner in which the halogens differ in the form of their ternary acids.

TABLE 41

TERNARY ACIDS OF THE HALOGENS

Acid		Salt	
Formula	Name	Formula	Name
$HClO$	Hypochlorous acid	Na^+ClO^-	Sodium hypochlorite
$HClO_2$	Chlorous acid	$Na^+ClO_2^-$	Sodium chlorite
$HClO_3$	Chloric acid	$Na^+ClO_3^-$	Sodium chlorate
$HClO_4$	Perchloric acid	$Na^+ClO_4^-$	Sodium perchlorate
$HBrO$	Hypobromous acid	Na^+BrO^-	Sodium hypobromite
$HBrO_3$	Bromic acid	$Na^+BrO_3^-$	Sodium bromate
HIO	Hypoiodous acid	Na^+IO^-	Sodium hypoiodite
HIO_3	Iodic acid	$Na^+IO_3^-$	Sodium iodate
HIO_4	meta-Per-iodic acid	$Na^+IO_4^-$	Sodium meta-periodate
H_5IO_6	ortho-Per-iodic acid	$Na_2^+H_3IO_6^=$	Disodium ortho-periodate

From Table 41 it is apparent that ternary acids of fluorine are unknown. There is, however, some evidence that salts of hypofluorous and fluoric acids exist in solution. The following discussion will be limited to the consideration of the acids of chlorine and their salts, since these compounds are by far the most common and useful.

The ternary acids of chlorine have certain properties in common. Thus, all four of these acids are rather unstable and are strong oxidizing agents. However, each of them forms salts that are markedly more stable than the corresponding acids.

Hypochlorous Acid and Its Salts. When chlorine gas is dissolved in water, the following equilibrium becomes established:

$$Cl_2^0 + HOH \rightleftharpoons H^+Cl^- + HClO$$

and the quantities of hydrochloric and hypochlorous acids present at equilibrium depend upon the temperature. The concentration of HClO in the equilibrium mixture may be increased by neutralizing the strong acid by the addition of a base such as sodium hydroxide. In practice, the best method for the formation of the hypochlorites and their parent acid is to pass chlorine into a *cold* solution of a strong base such as sodium hydroxide or calcium hydroxide.

$$Cl_2^0 + 2Na^+OH^- \rightarrow Na^+Cl^- + Na^+ClO^- + H_2O$$

A solution of hypochlorite having been obtained thus, a solution of hypochlorous acid may be obtained by acidification with a strong acid such as sulfuric.

$$Na^+ClO^- + H_2^+SO_4^= \rightarrow HClO + Na^+HSO_4^-$$

Both hypochlorous acid and the hypochlorites are relatively unstable and decompose readily with liberation of oxygen and the formation of chlorides. In fact, the acid is known only in solution. These compounds are excellent oxidizing agents; they are used as bleaching agents, as antiseptics, as disinfectants, and in the production of ethylene glycol. The commercial production of sodium hypochlorite by electrolysis has been described previously (Sec. 22.5).

Bleaching Powder. If, instead of cold sodium hydroxide, cold calcium hydroxide solution is used in reaction with chlorine, one obtains a solution containing calcium chloride and calcium hypochlorite.

$$2Cl_2^0 + 2Ca^{++}(OH)_2^- \rightarrow Ca^{++}Cl_2^- + Ca^{++}(ClO)_2^- + 2H_2O$$

If, on the other hand, chlorine gas is allowed to react with dry, solid calcium hydroxide, there is formed a compound having the formula, $CaOCl_2$. Commercially, this compound is known as *bleaching powder* and is regarded as being, at the same time, a salt of both hydrochloric and hypochlorous acids. This relationship may be clarified by the following formulas:

$Ca^{++}\begin{matrix}Cl^-\\Cl^-\end{matrix}$	$Ca^{++}\begin{matrix}ClO^-\\ClO^-\end{matrix}$	$Ca^{++}\begin{matrix}Cl^-\\ClO^-\end{matrix}$
Calcium chloride (a salt of hydrochloric acid)	Calcium hypochlorite (a salt of hypochlorous acid)	Calcium chloride hypochlorite (a salt of both hydrochloric and hypochlorous acids)

When bleaching powder is treated with a *strong* acid such as sulfuric, both hydrochloric and hypochlorous acids are liberated,

$$Ca^{++}\begin{matrix}Cl^-\\ClO^-\end{matrix} + H_2^+SO_4^= \rightarrow H^+Cl^- + HClO + Ca^{++}SO_4^=$$

and these acids interact to form chlorine,

$$H^+Cl^- + HClO \rightarrow Cl_2^0 + H_2O$$

By the use of a *weak* acid, however, only hypochlorous acid is liberated.

$$Ca^{++}\begin{matrix}Cl^{-}\\ \\ ClO^{-}\end{matrix} + H_2CO_3 \rightarrow HClO + Ca^{++}\begin{matrix}Cl^{-}\\ \\ HCO_3^{-}\end{matrix}$$

The ability of such solutions to act as bleaching agents is due to the liberated hypochlorous acid or to the oxygen formed by the decomposition of this acid,

$$HClO \rightarrow H^+Cl^- + [O]$$

where the enclosure of the symbol for oxygen implies the liberation of atomic (and consequently highly reactive) oxygen.

Chlorous Acid and Its Salts. As compared with the other acids of chlorine and their salts, chlorous acid and the chlorites are less well known and have no really important large-scale uses. Chlorous acid and chloric acid are formed together by the reaction between chlorine dioxide and water.

$$Cl_2O + H_2O \rightarrow HClO_2 + H^+ClO_3^-$$

Salts of these acids (chlorites and chlorates) may be formed by neutralizing the resulting solution with an appropriate base, and the two salts may then be separated.

Chloric Acid and Its Salts. This acid or its salts may be prepared by heating solutions of hypochlorous acid or hypochlorites,

$$3HClO + \text{heat} \rightarrow 2H^+Cl^- + H^+ClO_3^-$$

or

$$3Na^+ClO^- + \text{heat} \rightarrow 2Na^+Cl^- + Na^+ClO_3^-$$

The chlorates may be prepared directly by passing chlorine into a *hot* solution of a strong base, *e.g.*,

$$3Cl_2^0 + 6Na^+OH^- \rightarrow 5Na^+Cl^- + Na^+ClO_3^- + 3H_2O$$

Chloric acid may be produced (in solution) by treating an aqueous solution of a chlorite with a strong acid.

$$Na^+ClO_3^- + H^+HSO_4^- \rightarrow H^+ClO_3^- + Na^+HSO_4^-$$

Both chloric acid and chlorates are useful as oxidizing agents. Potassium chlorate is used in the manufacture of matches, fireworks, and explosives.

Perchloric Acid and Its Salts. The best method for the preparation of pure perchloric acid is first to prepare a salt of this acid by the action of heat upon a chlorate.

$$4Na^+ClO_3^- + \text{heat} \rightarrow Na^+Cl^- + 3Na^+ClO_4^-$$

The sodium perchlorate may be separated and used in the preparation of perchloric acid. It is preferable, however, to use barium perchlorate

$$Ba^{++}(ClO_4)_2^- + H_2^+SO_4^= \rightarrow \underline{Ba^{++}SO_4^=} + 2H^+ClO_4^-$$

since the salt formed as a by-product is insoluble and may be separated by filtration. If the water is evaporated from the resulting filtrate, one obtains a concentrated solution of perchloric acid but, because such solutions are explosive, it is best to allow the acid to remain in more dilute solutions. The uses of perchloric acid and its salts are similar to those given for chloric acid and the chlorates. In recent years, perchloric acid has come into general use as a reagent in analytical chemistry. Among the perchlorates, potassium perchlorate is of interest because it is one of the very few potassium salts that are substantially insoluble in water.

EXERCISES

1. Summarize briefly the manner in which the chemical and physical properties of the halogens change with increase in atomic number.
2. Which element in the halogen family would most likely be capable of losing one or more electrons to form a positive ion? Why?
3. List the chief natural source of each of the halogens.
4. By means of equations, give one method suited to the laboratory preparation of each of the halogens.
5. Describe the commercial procedure whereby bromine is extracted from sea water and include equations for the reactions involved.
6. If a plant were to be erected for the extraction of bromine from sea water, what would be the objection to locating the sea-water intake near the mouth of a river?
7. List important large-scale uses for each of (*a*) the halogens, (*b*) the hydrogen halides, (*c*) the ternary acids of chlorine, (*d*) the salts of the ternary acids of chlorine.
8. How do the elements of the halogen family differ with respect to (*a*) their tendencies toward combination with oxygen and (*b*) the stability of the oxides of the halogens?
9. (*a*) Which of the hydrogen halides may be produced conveniently by direct union of the elements? (*b*) Why may the others not be prepared conveniently in this manner?
10. If a hydrogen halide is to be prepared by the interaction of a salt and an acid, what properties must be possessed by the acid selected, and why?
11. Write equations to illustrate the reactions that occur during the etching of glass.
12. Since only two acids of bromine are known (*i.e.*, $HBrO$ and $HBrO_3$), is there any reason why $HBrO$ should not be called bromous acid rather than hypobromous acid?
13. What justification may be offered for giving to two different ternary acids of iodine (*i.e.*, HIO_4 and H_5IO_6) names involving the term per-iodic?
14. What evidence from Table 41 would indicate that the formula H_5IO_6 should not be written $HIO_4 \cdot 2H_2O$?

15. Compare the stability of (a) the ternary acids of chlorine and (b) hypochlorites, chlorites, chlorates, and perchlorates.

16. If sodium hypochlorite may be produced electrolytically as described in Sec. 22.5, suggest a change in experimental conditions which would make possible the production of sodium chlorate in a similar manner.

17. By means of equations, describe the commercial production of bleaching powder and show how this compound serves as a bleaching agent.

18. How will the equilibrium, $Cl_2^0 + HOH \rightleftharpoons H^+Cl^- + HClO$, be influenced by the addition of a strong acid? Why?

19. (a) Calculate the weight of sodium chlorate which may be produced from 1 ton of sodium hydroxide by the reaction between chlorine and sodium hydroxide. (b) Why is this reaction uneconomical from the standpoint of commercial use?

20. Inspect all the equations written in this chapter, make a list of all the oxidation-reduction reactions, and write each of these equations by the four-step procedure outlined in Chaps. XVIII and XXIV.

SUGGESTED READING

Journal of Chemical Education

Yost and Hatcher, The Chemistry of Fluorine, **10**, 330 (1933).

Baldwin, History of the Chlorine Industry, **4**, 313 (1927).

Baldwin, Uses of Chlorine, **4**, 454 (1927).

Bennett, Bleaching Photographs with Chlorine, **20**, 129 (1943).

Vincent, Fenrich, Synan, and Woodward, Two New Chlorine Compounds, **22**, 283 (1945).

Industrial and Engineering Chemistry

Cady, Rogers, and Carlson, Preparation of Fluorine, **34**, 443 (1942).

Hixon and Tenney, Chlorine and Salt Cake from Salt and Sulfur, **33**, 1472 (1941).

Stine, Recovery of Bromine from Sea Water, **21**, 434 (1929).

Stewart, Commercial Extraction of Bromine from Sea Water, **26**, 361 (1934).

White, Taylor, and Vincent, Chemistry of Chlorites, **34**, 782 (1942).

CHAPTER XXXI

COMMERCIAL PRODUCTION OF ACIDS AND BASES

Among the first chemicals that the student encounters in the laboratory are the common acids and bases. Since these materials are readily available and relatively inexpensive, the student is seldom called upon to prepare them in the laboratory. Nevertheless, one should become familiar with the manner in which these chemicals are produced commercially and with some of the problems that arise in connection with the conduct of chemical reactions on a large scale.

A few of the common acids and bases, together with certain salts that will be discussed in the next chapter, are produced in such very large quantities that they are commonly referred to as the *heavy* chemicals (*i.e.*, heavy in the sense of quantity production). In the discussion to follow, the methods used in the production of the more important of these chemicals will be considered briefly.

31.1. Development of Chemical Processes

Any considerable expenditure of effort, time, and money on the development of a commercial chemical process is based upon the premise that a market exists for the product (or products) or that the product has properties such that uses for it may be found and a market created. New uses may be found for compounds known to the chemist for many years but not previously produced on a large scale. On the other hand, it is often necessary for the chemist to discover hitherto unknown chemical compounds in order to find a substance which will fill an existing need.

Laboratory Investigation. New and potentially useful chemical changes are usually carried out first on a small scale in the laboratory. The discovery of such reactions or products may result from the desire to attain a preconceived objective, or it may be a by-product of experiments conducted for a totally different purpose. It is necessary then to determine by experiment the most favorable conditions (*i.e.*, temperature, pressure, concentration, catalysis, etc.) for the occurrence of the reactions in question. All of this knowledge must be acquired by the chemist before one can consider seriously the problem of large-scale utilization. If the laboratory investigations indicate probability

of success, there arises next the problem of adapting the process to a scale that will render economical the operation of a large chemical plant.

Process Development. It is not unusual to find that a reaction which proceeds smoothly when a few grams of the reactants are brought together may behave differently when much larger quantities of the reactants are involved. With drastic change in the quantities of materials, the reaction may occur no differently, more favorably, less favorably, or not at all. After the laboratory investigation has been completed, it is therefore necessary to determine whether the reaction will occur under controlled conditions on a larger scale. This phase of the work is usually conducted in a pilot plant or "semiworks" which is simply a miniature factory wherein the process in question is studied on a scale intermediate between that of the research laboratory and that of the anticipated manufacturing plant. When it is found that the reactions are not affected adversely by increased scale of operation, there arises the problem of the design and construction of all of the equipment that is necessary for the production and purification of the desired product or products in still larger quantities.

Chemical Economics. The preceding problems must be approached always in relation to economic considerations. One must consider the availability, location, and cost of raw materials. The cost of equipment and its maintenance, the cost of labor, power, etc., are only a few of the factors that govern the feasibility of the process. The actual location of the plant must be considered in relation to the cost of transportation of raw materials to the plant and of finished products to the market.

Ideally, a chemical reaction for use in a commercial process should yield only one product and this a pure one. However, this situation is infrequently realized and one must therefore consider the problem of utilization of by-products. The solution to this problem often makes the difference between success and failure. Finally, the feasibility of putting a chemical process into operation must be studied in relation to the existing or possible future competition, both domestic and foreign. Attention has been called previously to certain competitive chemical processes, and numerous additional cases will be cited in the following discussions.

ACIDS

Although a large number of acids are known to the chemist, only a few of them are produced by the chemical industries on a tonnage basis. Of these, the most important are hydrochloric, nitric, phosphoric, and sulfuric acids.

31.2. Hydrochloric Acid

At the present time, hydrochloric acid is produced commercially (*a*) from sodium chloride and sulfuric acid, (*b*) by the direct union of chlorine and hydrogen, and (*c*) as a by-product of other chemical processes. Although each of these sources contributes materially to the available supply of hydrochloric acid, the latter source is becoming increasingly important.

Preparation from Sodium Chloride and Sulfuric Acid. The chemical changes involved in this procedure are the same as those

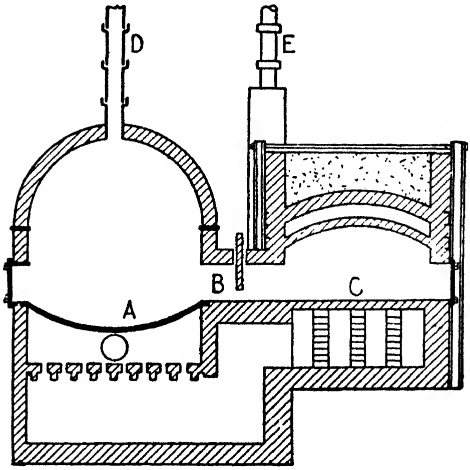


FIG. 133.—Furnace for the production of hydrochloric acid. (*Courtesy of Badger and Baker, Inorganic Chemical Technology, McGraw-Hill Book Company, Inc.*)

cited in connection with the discussion of the laboratory preparation of hydrogen chloride, *i.e.*,

$$Na^+Cl^- + H^+HSO_4^- \rightarrow Na^+HSO_4^- + \overline{HCl}$$
$$Na^+Cl^- + Na^+HSO_4^- \rightarrow Na_2^+SO_4^= + \overline{HCl}$$

The first of the reactions represented above takes place readily at only slightly elevated temperatures. The second, however, requires considerably higher temperatures which may approach (but should not exceed) the melting temperature of sodium sulfate, *i.e.*, 884°C. Although the type of apparatus used commercially may be illustrated by Fig. 133, other types of furnaces are also employed. A charge of salt and sulfuric acid is placed in the cast iron pan *A*, where the first step in the reaction occurs. This charge is then moved through the opening at *B* and onto the hearth represented at *C*, where, under the influence of higher temperatures, the second reaction occurs. In the meantime, another charge of salt and acid is introduced into the

pan A and is ready for transfer to C as soon as the preceding batch has reacted and the by-product sodium sulfate, known commercially as *salt cake*, has been removed. The hydrogen chloride so produced is removed (under suction) from the furnace through the flues D and E. Thereupon, these gases are cooled and absorbed in water to form hydrochloric acid solution of any desired concentration.

Preparation by Direct Union. Some of the chlorine produced as a by-product of the electrolytic production of sodium hydroxide (Sec. 22.5) is combined directly with hydrogen. The hydrogen is first fed into a quartz burner where the hydrogen is ignited in air, after which chlorine is introduced, and the hydrogen continues to burn in the atmosphere of chlorine to form substantially pure hydrogen chloride. There remains only the necessity of cooling the hydrogen chloride and dissolving it in water.

The simplicity of this process suggests that it should be used to the exclusion of the more involved procedure involving the reaction between salt and sulfuric acid. However, producers of sodium hydroxide do not use their by-product chlorine in this manner if there is a sufficient demand for the elemental chlorine as such. Furthermore, if a profitable market for sodium sulfate exists, it may be cheaper to produce hydrochloric acid from salt and sulfuric acid than from the elements. Finally, another competitive aspect to this situation arises in connection with the availability of by-product acid.

By-product Hydrochloric Acid. In the commercial production of many organic chemicals, hydrogen chloride is a by-product of the reactions employed. Thus, in the manufacture of chlorobenzene,

$$\begin{array}{ccccccc} C_6H_6 & + & \overline{Cl}{}_2^{\circ} & \rightarrow & C_6H_5Cl & + & \overline{HCl} \\ \text{Benzene} & & & & \text{Chloro-} & & \\ & & & & \text{benzene} & & \end{array}$$

hydrogen chloride is liberated. After removal of impurities, the hydrogen chloride is absorbed in water to form hydrochloric acid. Because so many reactions used in the organic chemical industries produce hydrogen chloride as a by-product, this promises to become the single most important source of supply of hydrochloric acid.

Properties and Uses of Commercial Hydrochloric Acid. The crude product obtained from salt and sulfuric acid contains ferric chloride as an impurity. This acid has a light yellow color (owing to the presence of ferric chloride) and is known as *muriatic acid.* The hydrochloric acid produced by the other two methods is colorless and usually of a high degree of purity. The purest commercial hydrochloric acid is that made by direct union of the elements.

Large quantities of hydrochloric acid are used in the metallurgical industries, particularly in the pickling of iron used for galvanizing and in the manufacture of wire. The processes of electroplating and etching also require considerable quantities of this acid. Most of the chemical industries use appreciable quantities of hydrochloric acid. The textile industries use this acid in dyeing and printing processes as well as in the manufacture of artificial silks and cotton goods. In the ceramic industries, hydrochloric acid is used in the purification of sand and clays used in the manufacture of glass and pottery. The acid is also used in the manufacture of dextrose, gelatin, glue, soaps, and a multitude of other chemical products.

31.3. Nitric Acid

So far as domestic production of nitric acid is concerned, only one process need be considered since all but a very small quantity of the nitric acid produced in this country is made by the catalytic oxidation of ammonia. In addition, a little-used method and one obsolete method will be discussed briefly.

Ostwald Process. This, the most widely used method for the production of nitric acid, depends upon the oxidation of ammonia by atmospheric oxygen in the presence of a catalyst consisting of gauze made of platinum or of platinum and rhodium. The reaction

$$4\overline{NH_3} + 5\overline{O_2} \rightarrow 4\overline{NO} + 6\overline{H_2O}$$

is carried out in a reaction chamber of the type shown in Fig. 134, at temperatures ranging from 600° to 900°. Upon leaving the reaction chamber the gases are cooled and more atmospheric oxygen is provided to permit the occurrence of the reaction

$$2\overline{NO} + \overline{O_2} \rightarrow 2\overline{NO_2}$$

The resulting nitrogen dioxide is then transferred to an absorption chamber and allowed to react with warm water.

$$3\overline{NO_2} + H_2O \rightarrow 2H^+NO_3^- + \overline{NO}$$

The nitric oxide liberated in this reaction is recovered and reconverted to nitrogen dioxide, and the nitric acid solution is concentrated and purified by distillation. Ordinarily, the nitric acid produced in this manner is about 50 per cent HNO_3. A more concentrated product may be obtained by distilling mixtures of nitric and sulfuric acids.

Production of Nitric Acid from Sodium Nitrate. Although widely used in the past, this method now accounts for less than 10 per cent of the nitric acid produced in the United States. In this process,

dried sodium nitrate and sulfuric acid are heated to about 150° in a retort.

$$Na^+NO_3^- + H^+HSO_4^- \rightarrow Na^+HSO_4^- + \overline{HNO_3}$$

The nitric acid vapors are led from the retort through a series of condensers and finally into absorption towers in which the acid is dis-

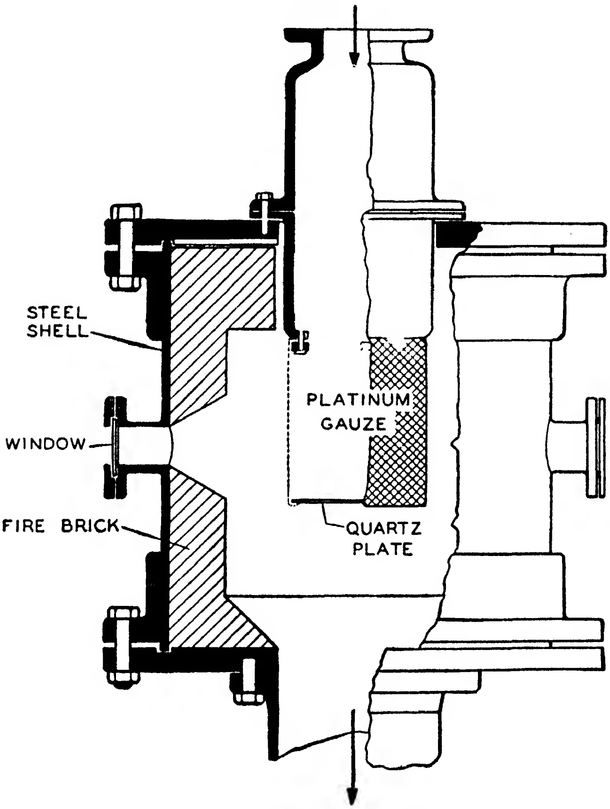


Fig. 134.—Catalyst chamber for the oxidation of ammonia. (*Courtesy of Badger and Baker, Inorganic Chemical Technology, McGraw-Hill Book Company, Inc.*)

solved in water. The by-product sodium hydrogen sulfate is known as *niter cake.* Although it would seem reasonable to expect that this material might be used in a second reaction

$$Na^+NO_3^- + Na^+HSO_4^- \rightarrow Na_2^+SO_4^= + \overline{HNO_3}$$

to produce more nitric acid, this reaction is not used commercially because the temperature required for its occurrence is sufficient to decompose the nitric acid thereby formed.

Arc Process. The arc or Birkeland-Eyde process was devised in Norway. This process is no longer used and is of interest here only because of certain unusual features. By this method, the endothermal reaction

$$\overline{N}_2 + \overline{O}_2 \rightleftharpoons 2\overline{NO} - 43{,}000 \text{ cal.}$$

utilized atmospheric oxygen and nitrogen. By means of a powerful magnetic field, an electric arc was spread into a large disk and air was blown through the flame at temperatures in excess of 3000°C. Under these conditions, approximately 4 per cent of the atmospheric nitrogen was converted to nitric oxide. After passing through the arc, the gases were cooled to 1000°, whereupon the nitric oxide reacted with more atmospheric oxygen to form nitrogen dioxide which was subsequently hydrated to form dilute nitric acid. Despite the fact that no expense is involved in the way of raw materials, the high cost of the electric power required made it impossible for this process to compete with the Ostwald process. However, an abundant supply of cheap hydroelectric power in Norway permitted the arc process to be operated economically for more than twenty-five years.

Uses of Nitric Acid. Most of the nitric acid produced is used in the manufacture of explosives. This is done either by converting the acid into its salts, the nitrates, or by using the acid in the nitration of certain organic compounds. Some of these nitrated organic substances are used as explosives while others are used in the manufacture of dyes, medicinals, etc. Nitric acid is used also in the production of fertilizers and many other chemicals.

31.4. Sulfuric Acid

Much has been written about the role of sulfuric acid as an index to national prosperity. Since this acid is generally considered to be one of the most important heavy chemicals and is used in so many of the industries, it is possible to evaluate trends in economic conditions by following the trends in the consumption of sulfuric acid. This applies not only to industry but also to agriculture because of the use of sulfuric acid in the manufacture of fertilizers.

There are two processes by which sulfuric acid is produced commercially. Because it can be described more simply, the newer process will be considered first.

Contact Process. This process has been in use for about fifty years and involves the use of the equipment shown diagrammatically by Fig. 135. The first step in the process is the formation of sulfur diox-

ide either by the burning of sulfur,

$$S + O_2 \rightarrow SO_2$$

or by the burning of *pyrite*, *galena*, *sphalerite*, or other sulfides. If sulfur is used, the sulfur dioxide requires but little purification but, if sulfide ores are employed, extensive and costly purification is necessary in order to remove arsenic and selenium oxides, halogens, and other impurities. After its formation in the sulfur burner, the sulfur dioxide

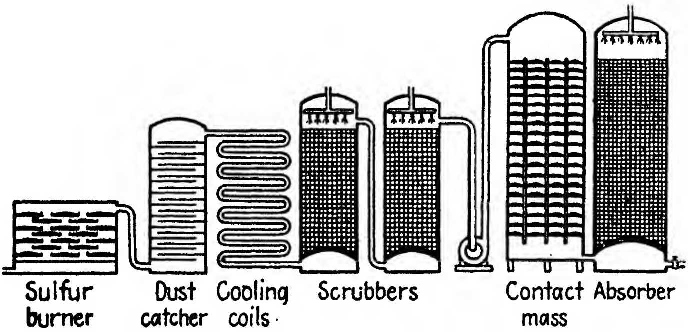


FIG. 135.—The contact process.

is passed successively through a dust catcher, cooling coils, and scrubbers. The gas is then led into a reaction chamber containing a suitable catalyst and maintained at 350° to 400°C. In this step, the reaction is

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{,}200 \text{ cal.}$$

The successful operation of the contact process became possible only through a knowledge of chemical equilibrium and the factors that influence such equilibrium. Since the reaction is exothermal, the temperature must be controlled carefully in order to avoid favoring the reverse reaction, *i.e.*, the decomposition of the desired sulfur trioxide. Although the forward reaction is favored by increase in pressure, this is not done in practice since 97 to 99 per cent conversion of sulfur dioxide to sulfur trioxide can be accomplished at the temperature specified above, provided suitable catalysts are used. The first catalyst used for this reaction consisted of finely divided platinum dispersed in asbestos, anhydrous magnesium sulfate, or silica gel. In recent years other catalysts have been discovered. Mixtures of ferric and cupric oxides are useful, but these are less efficient than platinum. Certain mixtures containing vanadium pentoxide (V_2O_5) and other compounds of vanadium appear to be as good or better than platinum. There has been much controversy over the relative merits of platinum

and vanadium catalysts, and only time will provide the answer as to which is best.

The sulfur trioxide is finally led into an absorber where *the gas is dissolved in concentrated sulfuric acid.* This is necessary since sulfur trioxide does not dissolve readily in water or in dilute sulfuric acid. However, after the trioxide has been dissolved in concentrated acid and this solution is added to water, the trioxide hydrates to form sulfuric acid.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Obviously, the concentration of the final product is governed by the quantity of water employed. In most contact plants, the quantity of water used is such that the final product is a concentrated acid (about 96 per cent of H_2SO_4).

The chief advantages of the contact process are (*a*) the high purity of the product and (*b*) the fact that the product is a concentrated acid. Disadvantageous factors are the high cost of the catalysts and the fact that, if sulfides are used as raw materials, costly purification of the sulfur dioxide is necessary because impurities such as arsenic trioxide and selenium dioxide "poison" the catalyst (*i.e.*, render the catalyst inactive). Platinum catalysts are particularly sensitive to these impurities while vanadium catalysts are claimed to be free from this disadvantage.

Lead-chamber Process. The essential features of the lead-chamber process are shown in Fig. 136. This process has been used for over seventy years, and the details of equipment and operation are essentially the same today as when the process was first designed.

Sulfur dioxide is produced by burning either sulfur or a sulfide such as pyrite in the furnace *O*. The dioxide is then mixed with the catalyst, NO, which may be prepared in either of two ways. In the older method, nitric acid vapor is formed in the "niter pot" *R* and, upon coming into contact with sulfur dioxide, nitric oxide is formed in accordance with the following equation:

$$2\overline{HNO_3} + 3\overline{SO_2} \rightarrow 2\overline{NO} + 3\overline{SO_3} + \overline{H_2O}$$

However, the more modern practice is to produce the nitric oxide by the catalytic oxidation of ammonia in the manner already described. The gases are then passed into the Glover tower *A*, where thorough mixing occurs. This tower (25 to 30 ft. high and 10 to 20 ft. in diameter) is usually constructed of heavy sheet lead or acidproof stoneware and is filled with quartz or stoneware tower packing. The gaseous mixture leaves the Glover tower at *B* and enters (at *C*) the

first of the lead-lined chambers from which the name of the process originated.

Although only two of these reaction chambers are shown in Fig. 136, from three to six are ordinarily used. The dimensions vary considerably and may be 50 to 150 ft. in length, 15 to 25 ft. in height, and 20 to 30 ft. in width. Although these may be of the same size, the first chamber is usually larger than the others. All these chambers are lined with sheet lead for the reason that this metal reacts with sulfuric acid to produce a tenacious coating of *insoluble* lead sulfate, which thereafter protects the underlying metallic lead from further attack by the acid.

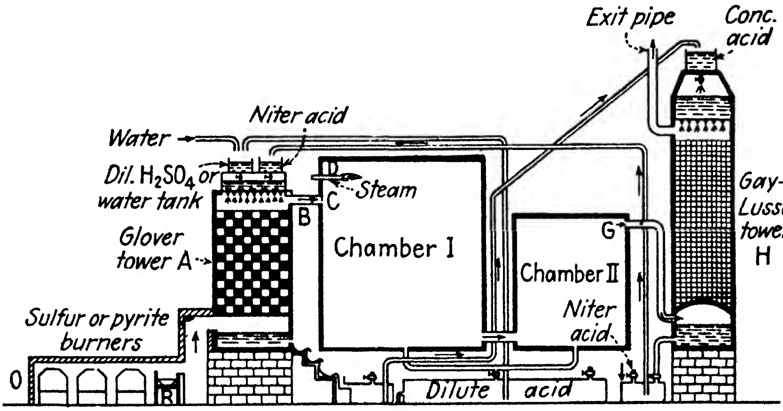


FIG. 136.—The lead chamber process.

In addition to the gaseous mixture that enters the chambers from the Glover tower, steam is introduced at *D*. Consequently, there are present all the reactants necessary for the formation of sulfuric acid. The reactions that occur in the chambers are rather complex and not fully understood. However, the following equations probably describe the principal changes. Nitrosyl sulfuric acid is formed by the reaction,

$$4\overline{SO_2} + 4\overline{NO} + 2\overline{H_2O} + 3\overline{O_2} \rightarrow 4 \begin{array}{ccc} O{=}N{-}O & & O \\ & \searrow \quad \nearrow & \\ & S & \\ & \swarrow \quad \searrow & \\ HO & & O \end{array}$$

This acid is converted to sulfuric acid either by hydrolysis

$$2 \begin{array}{ccc} O{=}N{-}O & & O \\ & \searrow \quad \nearrow & \\ & S & \\ & \swarrow \quad \searrow & \\ HO & & O \end{array} + HOH \rightarrow 2 \begin{array}{ccc} HO & & O \\ & \searrow \quad \nearrow & \\ & S & \\ & \swarrow \quad \searrow & \\ HO & & O \end{array} + \overline{NO} + \overline{NO_2}$$

or by reduction with sulfur dioxide,

$$2\begin{matrix} O{=}N{-}O & & O \\ & \diagdown \;\; \nearrow & \\ & S & \\ & \diagup \;\; \searrow & \\ HO & & O \end{matrix} + \overline{SO_2} + 2\overline{H_2O} \rightarrow 3\begin{matrix} HO & & O \\ & \diagdown \;\; \nearrow & \\ & S & \\ & \diagup \;\; \searrow & \\ HO & & O \end{matrix} + 2\overline{NO}$$

The dilute sulfuric acid is drained from the chambers and contains from 60 to 65 per cent of H_2SO_4. This acid is usually used in this concentration. Although there are several inconvenient and somewhat costly processes for the concentration of the lead-chamber acid, it is becoming increasingly difficult to concentrate this product economically in view of the ease with which concentrated sulfuric acid may be produced directly by the contact process.

From the foregoing equations, it is seen that nitric oxide is liberated upon formation of sulfuric acid. In order to avoid loss of this catalyst, the gases that leave the last chamber are led upward through the packed Gay-Lussac tower *H*, against a downward spray of concentrated sulfuric acid. Nitric oxide and nitrogen dioxide are dissolved by virtue of the re-formation of nitrosyl sulfuric acid.

$$\overline{NO} + \overline{NO_2} + 2H_2SO_4 \rightarrow 2\begin{matrix} O{=}N{-}O & & O \\ & \diagdown \;\; \nearrow & \\ & S & \\ & \diagup \;\; \searrow & \\ HO & & O \end{matrix} + H_2O$$

The resulting solution of nitrosyl sulfuric acid in concentrated sulfuric acid is withdrawn at the bottom of the Gay-Lussac tower, and this so-called *niter acid* is transferred by means of compressed air to the top of the Glover tower. Here it is allowed to mix with dilute acid or with water and this dilution, together with the rise in temperature due to both the heat of dilution and the contact with the hot gases streaming upward in the Glover tower, liberates nitric oxide and nitrogen dioxide. The catalyst is again made available and is ready to begin another cycle of operation. This recovery of catalyst is fairly efficient, but some of the oxides of nitrogen are lost and the required quantity of catalyst must be maintained by frequent introduction of fresh portions of nitric acid.

The lead-chamber process is more economical than the contact process but it produces a more dilute and less pure product. Thus, the chamber process can compete only in the market that can use a relatively impure and dilute acid. Although chamber acid plants now in use will undoubtedly be operated for many years to come, it seems probable that all sulfuric acid plants constructed in the future will employ the contact process or some still more efficient process.

Uses of Sulfuric Acid. It is not feasible here to do more than mention briefly the major uses of this acid. Of these, the use of dilute sulfuric acid in the manufacture of fertilizers (such as ammonium sulfate and primary calcium phosphate) is the most important from the standpoint of quantity of acid consumed. For these purposes, lead-chamber acid is adequate, and some fertilizer companies operate their own lead-chamber plants.

Large quantities of this acid are used in the metallurgical industries in the pickling of iron and steel (Sec. 27.9), in the production of zinc (Sec. 22.1), in the electrolytic refining of copper (Sec. 22.2) and other metals, in electroplating operations (Sec. 22.3), etc.

In the petroleum industry, sulfuric acid is used in refining processes to remove certain undesired components from crude petroleum. This acid is also employed in large quantities in the manufacture of explosives, paints, pigments, storage batteries, textiles (rayon and other cellulose products), dyes, drugs, etc.

In addition to the chemicals mentioned above, many others are manufactured by processes involving the use of sulfuric acid. Hydrochloric (Sec. 31.2) and nitric (Sec. 31.3) acids, which have already been discussed, may be cited as examples. Others include phosphoric acid (Sec. 31.5), sodium carbonate (Sec. 32.4), sulfates, alums, etc.

31.5. Phosphoric Acid

The old but still useful method for the production of phosphoric acid involves treatment of phosphate rock, bones, or other material containing phosphates, with sulfuric acid at elevated temperatures.

$$Ca_3^{++}(PO_4)_2^{\equiv} + 3H_2^{+}SO_4^{=} \rightarrow 2H_3PO_4 + 3Ca^{++}SO_4^{=}$$

Filtration provides a dilute solution of impure phosphoric acid which is then subjected to procedures designed to provide for both purification and concentration in whatever degree may be necessary.

The more modern process is based upon the previously described method for the production of elemental phosphorus (Sec. 28.9) from phosphate rock. Pure white phosphorus is oxidized to phosphorus pentoxide which is then hydrated to form phosphoric acid. This method is particularly useful where a concentrated product of high purity is sought.

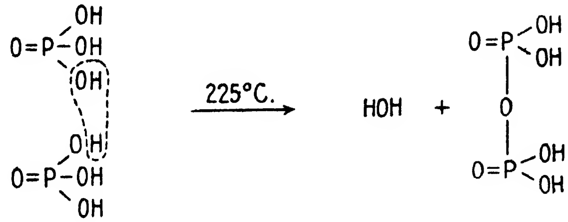
Uses of Phosphoric Acid. Although some phosphoric acid is used in the rustproofing of iron and in the manufacture of most high-grade phosphate fertilizers, the major uses for this acid are still concerned with the production of other chemicals. Baking powders,

phosphate sirups for use in making soft drinks, water-softening agents, etc., may be cited as typical examples.

From phosphoric acid (H_3PO_4) one may produce other acids of phosphorus. Thus, pyrophosphoric acid is formed by the mutual dehydration of 2 molecules of H_3PO_4 by application of heat,

$$2H_3PO_4 \xrightarrow{225°C.} H_4P_2O_7 + H_2O$$

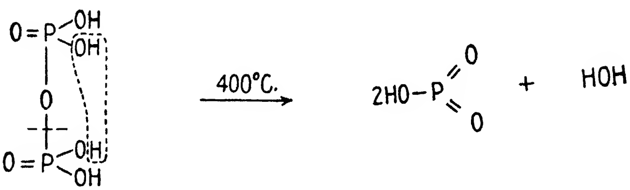
or



Further, an elevation of temperature to 400° converts pyrophosphoric acid to metaphosphoric acid,

$$H_4P_2O_7 \xrightarrow{400°C.} 2HPO_3 + H_2O$$

or



An inspection of the foregoing graphic formulas will show that the valence of phosphorus is the same in all three of these acids, *i.e.*, they are all phosphor*ic* acids. The prefixes *pyro-* and *meta-* are used in the naming of $H_4P_2O_7$ and HPO_3, respectively, while ordinary phosphoric acid (H_3PO_4) is more properly designated as *ortho*phosphoric acid.

Sodium hexametaphosphate [$(NaPO_3)_6$], which is the sodium salt of metaphosphoric acid, is an important chemical sold under the trade name of Calgon and used in the treatment of industrial water supplies.

BASES

In general, the commercial production of soluble bases does not introduce any problems that have not been considered heretofore. Accordingly, the methods used for the production of these compounds will be mentioned only briefly.

31.6. Sodium and Potassium Hydroxides

The production of sodium hydroxide by electrolysis has been described (Sec. 22.5) in sufficient detail, and this procedure serves equally well for the production of potassium hydroxide.

The older method for the production of sodium (or potassium hydroxide) is sometimes called the *chemical process* to distinguish it from electrolytic processes. The chemical process involves the treatment of sodium carbonate with calcium hydroxide.

$$Na_2^+CO_3^= + Ca^{++}(OH)_2^- \rightarrow 2Na^+OH^- + \underline{CaCO_3}$$

Removal of the precipitated calcium carbonate by filtration provides a filtrate consisting of sodium hydroxide solution, which may be used as such or which may be purified and evaporated to supply solid sodium hydroxide.

In recent years, the greatly increased demand for by-product chlorine has resulted in an increase in the production of sodium hydroxide by the electrolytic process. At the present time, the chemical and electrolytic processes produce about the same quantities of sodium hydroxide but, if the trend mentioned above continues, the chemical process will probably be used less in the future.

More than a million tons of sodium hydroxide are produced annually in the United States. This chemical is used in the manufacture of rayon and other textiles, pulp and paper, in the refining of petroleum and vegetable oils, in reclaiming used rubber, and in the production of a wide variety of other chemicals.

31.7. Calcium Hydroxide

This compound and the corresponding compounds of the related elements, barium and strontium, are produced by the hydration of their oxides. Thus, calcium hydroxide (slaked lime) is made by addition of water to calcium oxide (quicklime).

$$CaO + H_2O \rightarrow \underline{Ca^{++}(OH)_2^-}$$

If the quantity of water added is only that required in the reaction, the product is a white powder.

Because it is cheap, calcium hydroxide is used in many chemical processes that require a strong base. It is used in the production of sodium hydroxide (see above), ammonia, bleaching powder (Sec. 30.6), and many other chemicals. Calcium hydroxide is also used as an insecticide in the form of "lime-sulfur spray," in water softening, and in the production of numerous materials such as stucco and mortar which are so widely used in the building construction industries.

31.8. Ammonium Hydroxide

The production of ammonium hydroxide (*aqua ammonia*) is accomplished simply by dissolving gaseous ammonia in water. Under atmospheric pressure at 20°C., 710 liters of ammonia gas will dissolve in 1 liter of liquid water. The resulting solution is a weak base because of the occurrence, to a slight extent, of the forward reaction,

$$NH_3 + HOH \rightleftharpoons NH_4OH$$

Ammonium hydroxide is an important and useful reagent both in the industries and in the laboratory. Large quantities of dilute aqueous ammonia are used as a cleansing agent.

EXERCISES

1. Make a complete list of all the commercial processes discussed in this chapter and, for each process,
   (*a*) Write equations for the chemical changes involved.
   (*b*) Make a list of the raw materials required.
   (*c*) Make a list of the by-products, if any.
2. In the manufacture of sulfuric acid by the lead-chamber process, what is the function of (*a*) the Glover tower, (*b*) the Gay-Lussac tower?
3. (*a*) Describe briefly the electrolytic production of sodium hydroxide. (*b*) What bearing does this process have upon the choice of methods for the commercial production of hydrochloric acid?
4. List large-scale uses for (*a*) hydrochloric acid, (*b*) sulfuric acid, (*c*) phosphoric acid, (*d*) nitric acid, (*e*) sodium hydroxide, (*f*) calcium hydroxide.
5. Compare the contact and lead-chamber processes from the standpoint of (*a*) adaptability to different raw materials, (*b*) cost of operation, (*c*) nature of catalysts used, (*d*) quality of the product, (*e*) concentration of the product.
6. Explain why one is justified in looking upon nitric oxide (as it is used in the lead-chamber process) as falling within the scope of the usual definition of the term, catalyst.
7. Identify the terms: (*a*) niter cake, (*b*) muriatic acid, (*c*) salt cake, (*d*) Calgon, (*e*) slaked lime, (*f*) quicklime.
8. By means of equations involving graphic formulas, show the relationship between ortho-, pyro-, and meta-phosphoric acids.
9. Why is it more accurate to refer to a solution of ammonia in water as aqueous ammonia (or aqua ammonia) rather than ammonium hydroxide?
10. Phosphate rock deposits are located far from the market for phosphoric acid. If one were using the electric furnace process, how could one avoid the cost of transporting phosphoric acid to the existing market?

SUGGESTED READING

Journal of Chemical Education

TYLER, Some Economic Aspects of Chemical Process Development, **11**, **344** (1934).

LITTLE, Chemical Industry, **5**, **641** (1928).

HAYNES, Chemicals in Commerce, **12,** 103 (1935).

CONCANNON, Marketing American Chemicals, **6,** 1630 (1929).

BROWNE, Some Relations of Agricultural Chemical Research to National Prosperity, **6,** 665 (1929).

BAILAR, Variations in the Prices of Metals in the Last Twenty Years, **10,** 99 (1933).

Industrial and Engineering Chemistry

CHASE and PIERCE, The Manufacture of Sulfuric Acid by the Contact Process, **14,** 498 (1922).

SPANGLER, Recent Developments in the Manufacture of Sulfuric Acid, **21,** 417 (1929).

HOLMES, and ELDER, Vanadium Compounds as Catalysts for the Oxidation of Sulfur Dioxide, **22,** 471 (1930).

SCOTT and LAYFIELD, Characteristics of a Vanadium Catalyst and a New Catalyst for Sulfuric Acid, **23,** 617 (1931).

KALOUS, Improvements in Concentrating Sulfuric Acid, **35,** 387 (1943).

Chemical and Metallurgical Engineering

FAUSER, Concentrated Nitric Acid by Direct Synthesis, **39,** 430 (1932).

BRAHAM, Nitrates from the Air, **32,** 321 (1925).

CHAPTER XXXII

COMMERCIAL PRODUCTION AND UTILIZATION OF SALTS

A review of the commercial processes studied thus far will serve to illustrate the frequency with which salts serve as raw materials for the chemical industries. The salts so employed may be either naturally occurring materials or the principal products or by-products of other large-scale chemical operations. It is not feasible here to consider these matters either broadly or exhaustively; only a few of the more common types of salts will be considered briefly in the following sections.

CHLORIDES

The chlorides are, of course, the salts of hydrochloric acid and include many common and useful substances. Among others, sodium chloride, calcium chloride, zinc chloride, the chlorides of mercury, etc., are produced in considerable quantities and serve a variety of needs. Of these, only sodium chloride will be considered in detail.

32.1. Sodium Chloride

If one were to single out one chemical substance and designate it as being of first rank as a raw material for the chemical industries, that substance would probably be sodium chloride. The annual production of this material amounts to approximately 30 million tons, of which about one-fourth is produced in the United States. Other countries that produce large quantities of salt are Russia, Germany, France, Great Britain, India, and China. Within this country, the chief salt-producing areas are found in the states of Michigan, New York, Ohio, California, Louisiana, Kansas, West Virginia, and Texas. Salt is obtained from both underground deposits and the salt waters of the oceans and salt lakes.

Methods of Production. In any case, the method by which salt is produced from naturally occurring materials is determined by the quality of the product desired. In Louisiana and Texas, salt is produced by mining in a manner essentially the same as for any other underground mining operations. In these regions, a product of high purity (99.8 per cent of NaCl) is obtained directly. However, the salt

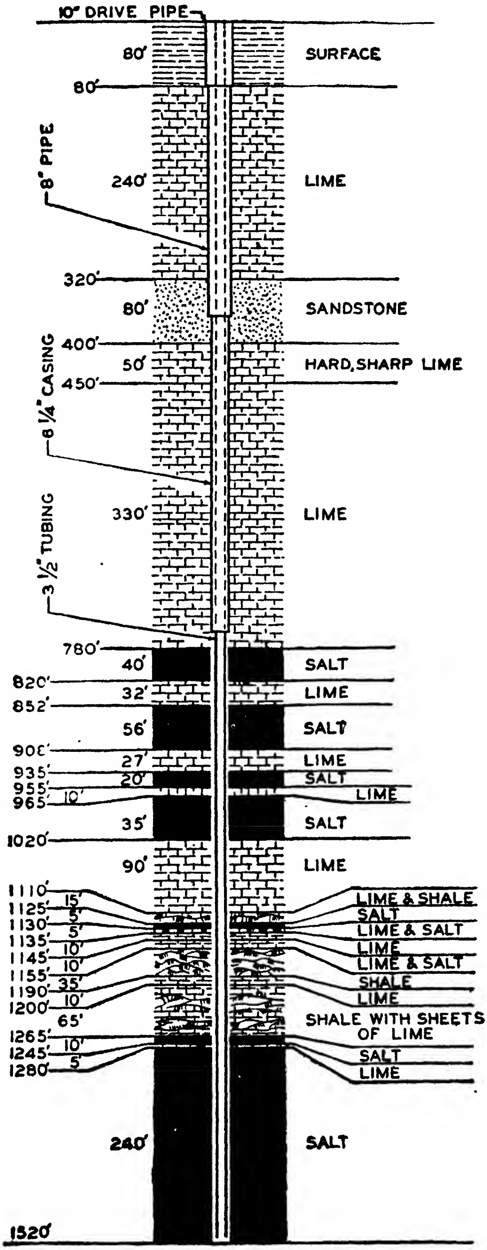


FIG. 137.—Section of a salt well. (*Courtesy of Badger and Baker, Inorganic Chemical Technology, McGraw-Hill Book Company, Inc.*)

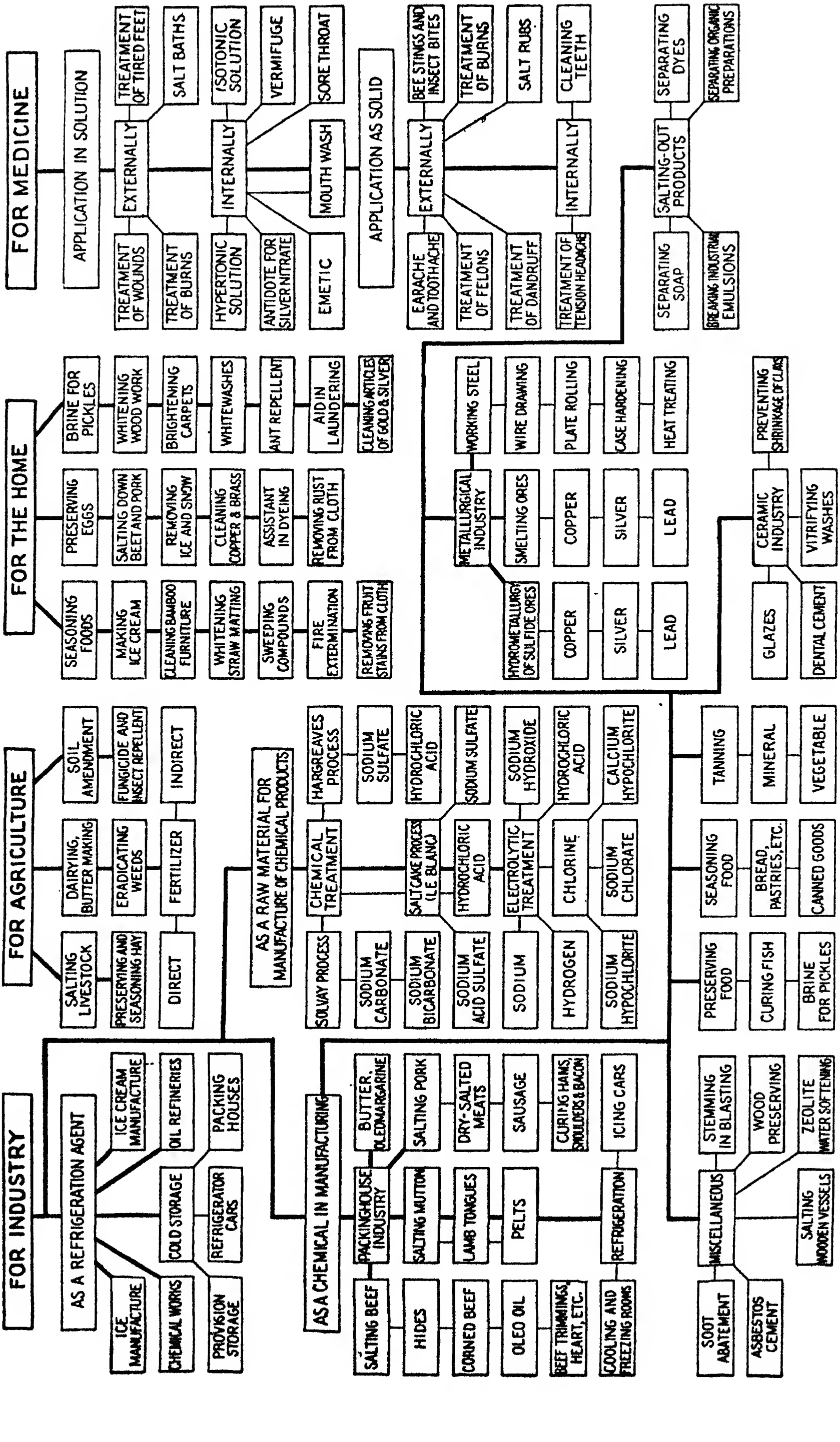


FIG. 138.—Uses of sodium chloride. *(Courtesy of Morton Salt Company.)*

produced in Michigan, New York, and Kansas by this type of mining is relatively less pure.

More commonly, salt is produced by the evaporation of natural brines which are formed by pumping water into salt wells and subsequently pumping the resulting brine to the surface. A diagram of a typical salt well is shown in Fig. 137. These brines usually contain sodium chloride as the main solute together with relatively small quantities of other salts, such as sodium and calcium sulfates, potassium and magnesium chlorides. Upon evaporation of the water, therefore, the resulting solid will consist largely of sodium chloride but, if a purer product is desired, the brine must be suitably treated to remove at least the major portion of the impurities.

Uses. The most familiar use of salt is in the seasoning of foods. Ordinary table salt is a relatively pure product, yet one that contains some hygroscopic magnesium chloride which, in humid weather, causes the salt to become moist and to pack. To prevent this, it is common practice to add inert materials such as starch, magnesia, or calcium phosphate, which form a protective coating on the surface of the salt crystals and thus retard the absorption of moisture from the surrounding atmosphere, or to add sodium hydrogen carbonate to convert the magnesium chloride into the nonhygroscopic carbonate. Iodized salt contains a small percentage (usually about 0.0025 to 0.0030 per cent) of potassium iodide.

As already indicated, vast quantities of salt are used in the chemical industries in the production of other chemicals. Including these indirect as well as the direct uses, there are more than a thousand more or less distinct uses for this chemical. Some of these uses are summarized in Fig. 138.

CARBONATES

Since carbonates are salts of carbonic acid, both the acid salts and the normal salts are included under this heading. Of the many known salts that belong to this class, those most extensively used in the chemical industries are calcium carbonate and the carbonates of sodium.

32.2. Calcium Carbonate

In the form of ordinary *limestone*, calcium carbonate is a very abundant raw material. In addition to calcium carbonate, limestone contains a variety of impurities, notably compounds of iron, aluminum, magnesium, silicon, etc. The mineral *dolomite* is the double carbonate of calcium and magnesium ($CaCO_3 \cdot MgCO_3$). Eggshells, oystershells, coral, and similar materials contain high percentages of calcium car-

bonate. The mineral *calcite* is nearly pure calcium carbonate. Including all sources, about 100 million tons of limestone are mined annually in the United States. Although this material is produced in practically all the 48 states, Ohio, Illinois, Michigan, Pennsylvania, and New York are the largest producers.

Uses. In the form of large compact blocks of ordinary limestone or in the form known as *marble*, large quantities of calcium carbonate are used as building stones. Limestone is also used in the building of roads, in the manufacture of cement, in the metallurgical industries, and as a fertilizer on acidic soils.

Calcium carbonate in the form of limestone is the source of all of the lime and much of the carbon dioxide produced in this country. When calcium carbonate is heated to about 900°, it decomposes as shown by the following equation:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

and this reversible reaction proceeds to completion if the gaseous carbon dioxide is progressively removed as the reaction proceeds.

On a commercial scale, lime is produced by heating crushed limestone in large furnaces or *kilns* of the type shown in Fig. 139. The usual lime kiln is about 50 ft. in height and is constructed so that heat is supplied by fireboxes located near the bottom of the kiln. A current of air is admitted at the bottom, and this air serves to cool the lime near the bottom of the kiln and provides oxygen for the burning of the fuel used in the fireboxes. Further, this upward flow of gas serves to carry out the carbon dioxide as rapidly as it is liberated. The residual solid lime (quicklime) is removed periodically at the bottom, and new charges of limestone are admitted at the top.

When quicklime (CaO) is brought into contact with water, calcium hydroxide (slaked lime) is formed and heat is liberated in the process.

$$CaO + H_2O \rightleftharpoons Ca^{++}(OH)_2^-$$

32.3. Sodium Hydrogen Carbonate

Although sodium hydrogen carbonate (commonly known as *sodium bicarbonate*) is a component of the naturally occurring double salt $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, known as *trona*, practically all of the commercial product is manufactured from sodium chloride, ammonia, and carbon dioxide by the Solvay process, which was devised in 1863 by Ernest and Alfred Solvay, two Belgian chemists. It is very widely used and is the source of most of the world's supply of sodium hydrogen carbonate (and, as will be shown later, of normal sodium carbonate as well). The essential chemical changes involved in the Solvay process

are

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$
$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$NH_4OH + H_2CO_3 \rightarrow H_2O + NH_4^+HCO_3^-$$
$$NH_4^+HCO_3^- + Na^+Cl^- \rightarrow \underline{NaHCO_3} + NH_4^+Cl^-$$

The precipitation of $NaHCO_3$ from aqueous solutions is carried out below 15°C., under which conditions the acid carbonate is only slightly soluble. The product so obtained is usually quite pure.

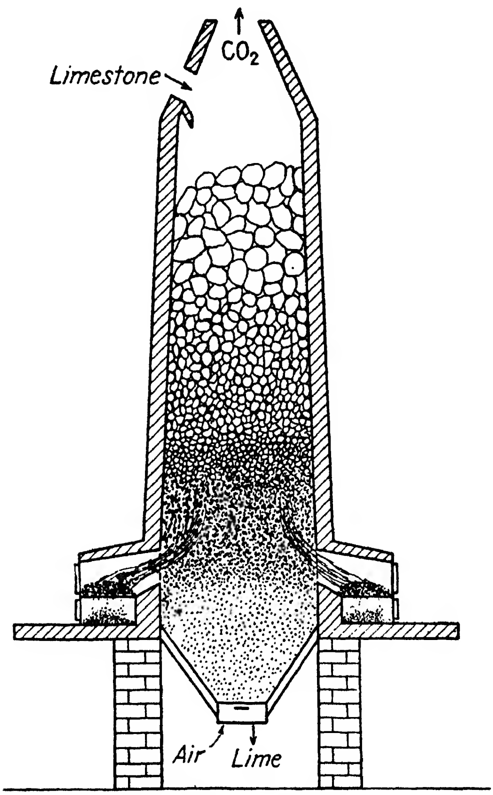


FIG. 139.—Lime kiln.

It will be noted that ammonia used in the Solvay process appears at the end of the above series of reactions in the form of the by-product, ammonium chloride. The ammonia is recovered by treating the solution (containing the ammonium chloride) with lime.

$$CaO + H_2O \rightarrow Ca^{++}(OH)_2^-$$
$$2NH_4^+Cl^- + Ca^{++}(OH)_2^- \rightarrow 2\overline{NH_3} + 2H_2O + Ca^{++}Cl_2^-$$

The over-all efficiency of recovery of ammonia is commonly in the

neighborhood of 99 per cent; hence, most of the ammonia is used over and over again in the process. The lime used in the recovery of ammonia is ordinarily produced by the thermal decomposition of limestone.

$$CaCO_3 \rightarrow CaO + \overline{CO_2}$$

a reaction that also furnishes carbon dioxide, which is one of the raw materials used in the main process

32.4. Sodium Carbonate

The normal carbonate (commonly known as *soda*) occurs in nature as *natron* ($Na_2CO_3 \cdot 10H_2O$), *thermonatrite* ($Na_2CO_3 \cdot H_2O$), *trona* ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), and as *soda brine.* Deposits of these materials are widely distributed and some of the more important deposits are found in the United States, Africa, China, Siberia, South America, and Central Europe. In the United States, the most important sources are those of Owens Lake and Searles Lake in California and the Green River deposits in Wyoming. Despite the existence of these minerals in nature, only about 3 per cent of our domestic supply of soda comes from these sources. In fact, the total tonnage of soda produced from all natural sources is not very large when compared to the tonnage produced by the Solvay and LeBlanc processes.

Solvay Process. Sodium hydrogen carbonate having been produced by the Solvay process as described in Sec. 32.3, the normal carbonate is made by heating the acid salt to 175° to 190°C. in a rotary drier.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + \overline{CO_2}$$

Of course, the liberated carbon dioxide is returned to the main process and used again to make more of the acid salt.

LeBlanc Process. In 1775 the French Academy of Sciences offered a prize of 100,000 francs to anyone who could devise a process for the production of soda from raw materials found in France. The prize was claimed (but never received) in 1791 by Nicolas LeBlanc, who used ordinary salt, sulfuric acid, coke, and limestone as the starting materials. The essential reactions involved are

$$\begin{aligned} NaCl + H_2SO_4 &\rightarrow NaHSO_4 + \overline{HCl} \\ NaCl + NaHSO_4 &\rightarrow Na_2SO_4 + \overline{HCl} \\ Na_2SO_4 + 2C &\rightarrow Na_2S + 2\overline{CO_2} \\ Na_2S + CaCO_3 &\rightarrow Na_2CO_3 + CaS \end{aligned}$$

The first of these reactions occurs at ordinary temperatures, some heating is required for completion of the second, while the third and fourth are carried out in a furnace at about 1000°C.

The sodium carbonate is extracted in water, purified, and sold as *sal soda* ($Na_2CO_3 \cdot 10H_2O$), *glassmaker's soda* ($Na_2CO_3 \cdot H_2O$) or as the anhydrous salt (Na_2CO_3) which is commonly known as *soda ash.*

Further details of the LeBlanc process are omitted here for the reason that it is primarily of historical interest. The Solvay process is so superior in all respects that the LeBlanc process is used little, if at all, at the present time and has never been used in the United States. It is of interest, however, to point out that, while the primary product of the LeBlanc process is the normal carbonate, it may be converted to the acid carbonate by treatment with carbon dioxide in aqueous solutions.

$$Na_2^+CO_3^= + H_2O + CO_2 \rightarrow 2Na^+HCO_3^-$$

Uses of Sodium Carbonate. In its various forms, more than 3 million tons of soda are used annually. Approximately one-half of this amount is used in the production of other chemicals, about one-fourth is used in the manufacture of glass, and the remainder is used for a variety of purposes including the production of pulp and paper, soap, textile products, and petroleum. Appreciable quantities of sodium carbonate are also used in the "softening" of natural waters.

32.5. Chemical Treatment of Natural Waters

Both directly and indirectly, the general problem of purification and treatment of natural waters is related to the chemical and physical properties of the normal and acid salts of carbonic acid.

The common impurities in natural waters consist of suspended solid organic and inorganic materials and of certain dissolved salts, particularly the acid carbonates, chlorides, and sulfates of sodium, calcium, and magnesium. The solid matter may be removed by filtration, the presence of limited quantities of sodium salts is not objectionable, and the calcium and magnesium salts are eliminated only through appropriate chemical treatment. The ions that are most objectionable are Ca^{++}, Mg^{++}, and HCO_3^-. If calcium and magnesium ions are allowed to remain in water for use in laundries, they react with soap to form insoluble salts. Thus, a considerable quantity of soap may have to be added to "soften" the water and no cleansing action is secured until all the calcium and magnesium ions have been precipitated. This results not only in an enormous waste of soap but also in the appearance of an undesirable and unsightly scum of insoluble salts. If Ca^{++} and Mg^{++} ions together with HCO_3^- ions are permitted to remain in water for use in steam boilers, hot-water heating pipes or radiators, conversion to insoluble normal carbonates results in the formation of

scale or incrustation known as *boiler scale* (Fig. 140). The formation of these deposits not only results in lowered efficiency of the boilers or heating systems but also may lead to serious explosions if the scale deposits become excessive.

The particular chemical treatment to which natural waters are subjected depends upon the use or uses for which the water is intended. If water is intended for human consumption, provision must be made for the elimination of significant quantities of harmful bacteria. This is accomplished in part by the chemical treatment designed to remove "hardness," but it is accomplished most effectively by treatment with chlorine, the characteristic odor of which is frequently detectable in municipal water supplies.

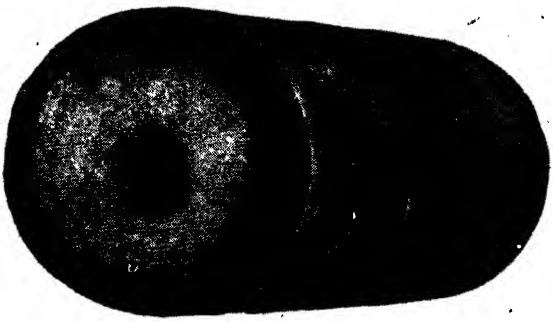


FIG. 140.—A boiler tube containing a heavy deposit of scale. (*Courtesy of The Permutit Company.*)

Temporary Hardness. Probably because of the ease with which these impurities may be removed, the acid carbonates of calcium and magnesium (and in some cases ferrous iron) are said to constitute *temporary hardness* in water. This type of hardness may be removed by boiling the water, whereupon the soluble acid carbonates are converted to the insoluble normal carbonates which may be removed by filtration.

$$Ca^{++}(HCO_3)_2^- \rightarrow \underline{CaCO_3} + H_2O + \overline{CO_2}$$
$$Mg^{++}(HCO)_2^- \rightarrow \underline{MgCO_3} + H_2O + \overline{CO_2}$$

Although this method could be used on a small scale, its use in the treatment of municipal water supplies would involve prohibitive costs. Accordingly, advantage is taken of the fact that the objectionable ions may be removed by treatment with a base such as calcium hydroxide (slaked lime).

$$\mathrm{Ca^{++}(HCO_3)_2^- + Ca^{++}(OH)_2^- \rightarrow 2H_2O + \underline{2CaCO_3}}$$
$$\mathrm{Mg^{++}(HCO_3)_2^- + Ca^{++}(OH)_2^- \rightarrow 2H_2O + \underline{MgCO_3} + \underline{CaCO_3}}$$

Permanent Hardness. Although the use of the adjective permanent is inappropriate, *permanent hardness* is the term commonly used to describe the hardness due to the presence of the chlorides and sulfates of calcium and magnesium. This type of hardness may be removed by treatment with sodium carbonate.

$$\mathrm{Ca^{++}Cl_2^- + Na_2^+CO_3^= \rightarrow \underline{CaCO_3} + 2Na^+Cl^-}$$
$$\mathrm{Mg^{++}SO_4^= + Na_2^+CO_3^= \rightarrow \underline{MgCO_3} + Na_2^+SO_4^=}$$

The sodium carbonate is usually added in the form of *soda ash.*

Lime-soda Process. Combination of the use of slaked lime for the removal of temporary hardness and sodium carbonate for the removal of permanent hardness constitutes the *lime-soda process* for the softening of natural waters. This method is commonly used in municipal water-treatment plants and is a cheap and yet fairly effective process. If sufficient time can be allowed, the insoluble carbonates may be permitted to settle out in settling basins or more rapidly removed by means of filters. Frequently, iron or aluminum salts are added, and these hydrolyze to form gelatinous precipitates of ferric or aluminum hydroxides. As these precipitates settle slowly, they carry with them the insoluble normal carbonates, as well as any other suspended matter such as sand, clay, or organic matter which otherwise is sometimes slow in settling.

Zeolite Processes. In recent years there has been developed a simple and remarkably effective method for the removal of hardness from water. This scheme utilizes a reversible metathetical reaction between calcium and magnesium salts and substances called *zeolites.* These materials are natural or artificial sodium aluminum silicates (for example, $Na_2Al_2Si_2O_8$) which may be considered as complex salts of orthosilicic acid (H_4SiO_4). When hard water is allowed to flow through a bed of a granular zeolite (Fig. 141), reactions of the type illustrated by the following equations result:

$$\mathrm{Ca^{++}Cl_2^- + \underline{Na_2Al_2Si_2O_8} \rightleftharpoons 2Na^+Cl^- + \underline{CaAl_2Si_2O_8}}$$
$$\mathrm{Mg^{++}SO_4^= + \underline{Na_2Al_2Si_2O_8} \rightleftharpoons Na_2^+SO_4^= + \underline{MgAl_2Si_2O_8}}$$
$$\mathrm{Ca^{++}(HCO_3)_2^- + \underline{Na_2Al_2Si_2O_8} \rightleftharpoons 2Na^+HCO_3^- + \underline{CaAl_2Si_2O_8}}$$

Thus, both temporary and permanent hardness are removed almost completely by an exchange of sodium ions for calcium and magnesium ions. When the sodium in the original zeolite has all been replaced by calcium or magnesium, the sodium zeolite is regenerated by allowing

a concentrated salt solution to flow through the bed. This treatment, in accordance with the law of mass action, reverses the above reactions and the zeolite bed is restored to its original condition and, by periodic regeneration of this sort, the zeolite may be used repeatedly over long periods of time. The future will undoubtedly see a much more widespread use of the zeolite process or processes depending upon the use of

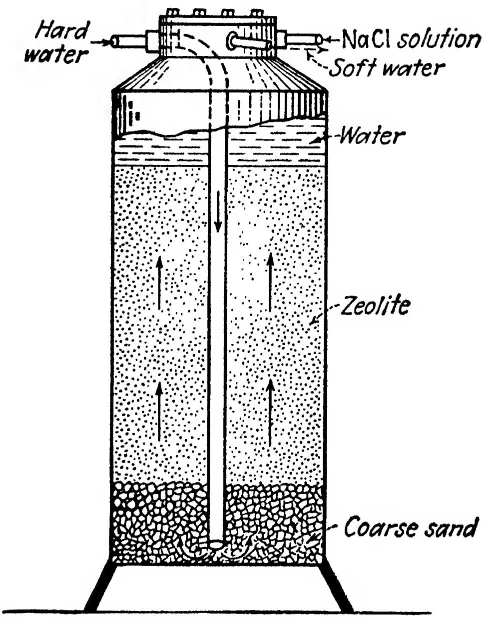


Fig. 141.—The zeolite process for the removal of hardness from water.

other synthetic materials which behave in a manner similar to that of the zeolites. Still other synthetic materials are now available which permit the removal of anionic constituents.

NITRATES

Reference has already been made to the use of nitrates as raw materials for the production of nitric acid (Sec. 31.3). On a quantity basis, however, this application accounts for only a relatively small proportion of the annual consumption of these salts by the chemical industries.

32.6. Production and Uses of Nitrates

The chief source of naturally occurring nitrates is a rather sharply limited area along the arid coastal range of Chile. The ore in these deposits is known as *caliche* and consists principally of sodium nitrate,

which is commonly known as *Chile saltpeter*. The deposits range in depth from 5 to 15 ft. and are up to 200 miles in length. Sodium nitrate is removed from the crude ore (about 60 per cent of $NaNO_3$) by leaching with water, after which the resulting solutions are evaporated. The annual production of Chile saltpeter amounts to more than 3 million tons.

Since practically all nitrates are soluble in water, one would not expect to find extensive deposits of these salts in nature excepting in arid or semiarid regions. In addition to the nitrate deposits in Chile, limited quantities of potassium nitrate occur in the Orient. Most of the potassium nitrate used at the present time is made by the metathetical reaction between sodium nitrate and potassium chloride,

$$Na^+NO_3^- + K^+Cl^- \rightarrow K^+NO_3^- + \underline{Na^+Cl^-}$$

a reaction that may be caused to proceed to completion by taking advantage of the fact that sodium chloride is much less soluble in water than potassium nitrate (see Fig. 43). The bulk of the available supply of nitrates, however, is produced directly or indirectly from nitric acid.

Nitrate Fertilizers. Of the numerous elements that must be present to support the growth of plants in the soil, nitrogen, phosphorus, and potassium are those most commonly added to the soil in the form of commercial fertilizers. Nitrates are often used as a source of nitrogen, and the nitrates most used in fertilizer mixtures are those of sodium, calcium, and potassium. The latter has the obvious advantage of supplying both nitrogen and potassium and hence an unusually high fertilization value on a comparative weight basis.

The use of nitrates in the maintenance of soil fertility is a part of the general problem of nitrogen fixation (Sec. 28.5). Accordingly, any process that accomplishes the conversion of atmospheric nitrogen to ammonia or nitric acid is a potential source of nitrates for use as fertilizers. It is evident that nitrates (either natural or synthetic) for use as fertilizers need not be of a high degree of purity.

Nitrate Explosives. The term *explosion* is applied to the effect produced by a sudden change in the pressure of one or more gases. This may be the result of either chemical or physical changes; *i.e.*, the sudden liberation or absorption of gases in chemical reactions or the sudden formation of gases from either liquids or solids. Because certain nitrates decompose readily with liberation of gaseous products, these substances are useful in the compounding of a variety of commercial explosives.

Ammonium nitrate is stable under ordinary atmospheric conditions and may be handled safely in small quantities, even at elevated tem-

peratures. When the dry salt is heated, it decomposes with liberation of nitrous oxide and water,

$$NH_4NO_3 \rightarrow \overline{N_2O} + 2\overline{H_2O}$$

and this reaction provides probably the most convenient laboratory method for the preparation of nitrous oxide. If solid ammonium nitrate is detonated, the decomposition occurs with explosive violence. A number of high explosives consist of mixtures containing ammonium nitrate, *e.g.*, ammonal, amatol, etc.

Potassium nitrate (together with sulfur and charcoal) is used in the manufacture of gunpowder ("black powder"). When such a mixture is ignited by means of a spark, both gaseous and solid decomposition products are produced in the resulting explosive reaction which is quite complex. Black powder is used in the manufacture of ammunition for small firearms, in the production of time fuses, and as a blasting powder in mining operations.

PHOSPHATES

Since there are three common acids of phosphorus (Sec. 31.5), the normal and acid salts of which are phosphates, it follows that this is indeed a large group of salts. This fact becomes all the more evident if the salts of the less common acids of pentavalent phosphorus are included. Of this large number of salts, however, only a few may be classed as important commercial chemicals.

32.7. Orthophosphates

Aside from their use as reagents in the chemical laboratory, most of the possible metal salts of orthophosphoric acid have not found extensive application in the chemical industries. There are, however, a few notable exceptions. The normal phosphates of the alkali metals are readily soluble in water and are used to a considerable extent as cleansing agents and as water softeners.

Primary calcium phosphate [$Ca(H_2PO_4)_2$] is used in the manufacture of certain baking powders. In the presence of moisture, the acid phosphate reacts with sodium hydrogen carbonate (another constituent of such powders) to produce gaseous carbon dioxide which causes the dough to "rise."

Phosphate Fertilizers. From the extensive phosphate rock deposits in Tennessee, South Carolina, Florida, Idaho, and Montana, approximately 3 million tons of ore are used annually in the manufacture of fertilizers. The chief phosphate present in this rock is the normal calcium salt [$Ca_3(PO_4)_2$]. Because of its insolubility, this

compound is not very useful as a fertilizer. If a phosphorus compound is to provide phosphorus that can be assimilated by growing plants, the compound must be one that is appreciably soluble in the soil moisture.

The utilization of tricalcium phosphate therefore requires its conversion into a soluble salt. This is accomplished by treating the normal phosphate with dilute sulfuric acid (lead-chamber acid) and thereby producing the soluble primary calcium phosphate.

$$\underline{Ca_3(PO_4)_2} + 2H_2^+SO_4^= \rightarrow Ca^{++}(H_2PO_4)_2^- + \underline{2CaSO_4}$$

The resulting *mixlure* of calcium dihydrogen phosphate and calcium phosphate is sold as "superphosphate" fertilizer. It is of interest to note that the production of calcium sulfate is avoided by using phosphoric acid rather than sulfuric.

$$\underline{Ca_3(PO_4)_2} + 4H_3^+PO_4^{\equiv} \rightarrow 3Ca^{++}(H_2PO_4)_2^-$$

Although superphosphate fertilizer provides available phosphorus, it is advantageous at the same time to provide other needed elements such as nitrogen and potassium. Thus diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] provides both nitrogen and phosphorus, while potassium ammonium phosphate [$K(NH_4)HPO_4$] makes available the three elements most needed in the maintenance of soil fertility. Compounds of this type are coming into more general use, and this trend will undoubtedly continue.

32.8. Metaphosphates

The salts of metaphosphoric acid may be produced in a number of ways, but most conveniently by heating the appropriate dihydrogen orthophosphate, thus,

$$NaH_2PO_4 \rightarrow \overline{H_2O} + NaPO_3$$

In the form of sodium hexametaphosphate [$(NaPO_3)_6$], which is known by the trade name *Calgon*, this metaphosphate is used in water treatment (to prevent the precipitation of small quantities of calcium and magnesium salts not removed in the lime-soda process) and to dissolve scale that has formed in boilers, water pipes, etc.

32.9. Pyrophosphates

The pyrophosphates may be formed by heating the corresponding monohydrogen orthophosphates.

$$2Na_2HPO_4 \rightarrow \overline{H_2O} + Na_4P_2O_7$$

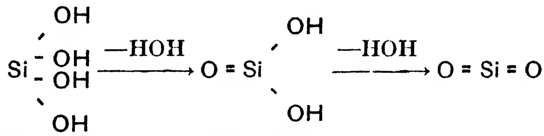
Although there are no really large-scale uses for pyrophosphates, small quantities are employed (in solution) to dissolve boiler scale.

SILICATES

Because the class of salts known as *silicates* includes so many familiar naturally occurring materials, some attention is given here to the chemical character of these salts. Although the silicates are important raw materials for a number of industries, the commercial applications of silicates are mentioned only briefly.

32.10. Salts of Silicic Acids

The silicates may be looked upon as salts of a considerable variety of silicic acids, some of which are far more complex than any acids studied thus far. The two simplest acids of silicon are orthosilicic and metasilicic acids. The relationship between these two acids and their anhydride may be shown as follows:



Orthosilicic acid — Metasilicic acid — Silicon dioxide

Examples of common orthosilicates include *zircon* ($ZrSiO_4$), *mica* [$KH_2Al_3(SiO_4)_3$], and *kaolin* [$H_2Al_2(SiO_4)_2 \cdot H_2O$]. The minerals *beryl* [$Be_3Al_2(SiO_3)_6$] and *asbestos* [$Mg_3Ca(SiO_3)_4$] are examples of common metasilicates.

More complex silicic acids, known only in the form of their salts, may be considered as derived from orthosilicic acid by processes of selective dehydration. Thus, one may represent the formation of series of disilicic acids,

$$2H_4SiO_4 \xrightarrow{-HOH} H_6Si_2O_7 \xrightarrow{-HOH} H_4Si_2O_6 \xrightarrow{-HOH} H_2Si_2O_5$$

or trisilicic acids,

$$3H_4SiO_4 \xrightarrow{-HOH} H_{10}Si_3O_{11} \xrightarrow{-HOH} H_8Si_3O_{10} \xrightarrow{-HOH} H_6Si_3O_9, \text{ etc.}$$

Serpentine ($Mg_3Si_2O_7 \cdot 2H_2O$) is a disilicate and *orthoclase* ($KAlSi_3O_8$) is a trisilicate.

Water Glass. A familiar and useful silicate is that known as *water glass.* Although the commercial product consists of a rather complex mixture of silicates, water glass is commonly represented by

the formula for the normal sodium salt of metasilicic acid, *i.e.*, Na_2SiO_3. This material is produced by heating sand with sodium hydroxide under pressure,

$$SiO_2 + 2Na^+OH^- \rightarrow 2H_2O + Na_2^+SiO_3^=$$

or by fusing sand with sodium carbonate,

$$SiO_2 + Na_2^+CO_3^= \rightarrow Na_2^+SiO_3^= + CO_2$$

Water glass is usually sold in the form of clear sirupy solutions and is used as an egg preservative, as a cement in the manufacture of cardboard boxes, as a fireproofing agent, in the manufacture of soaps and cleaners, etc.

Ceramic Industries. The chemical and physical properties of silicates are utilized to advantage in a group of industries which collectively may be termed the *ceramic* industries. These are concerned with the manufacture of products such as cement, glass, porcelain, bricks, tile, terra cotta, and enamels. All these industries utilize a wide variety of complex naturally occurring silicates.

EXERCISES

1. In what regions in the United States is sodium chloride found in nature in the most important commerical quantities?
2. What constituent causes table salt to become moist? By what chemical or physical means may this be prevented?
3. List 10 important chemicals which are produced using common salt either directly or indirectly as a raw material.
4. What are the chief impurities in crude sodium chloride? Suggest chemical reactions by means of which these ions might be removed without introducing other impurities that could not be removed readily.
5. In general terms, what types of process are used in the commercial production of sodium chloride?
6. Distinguish between (*a*) limestone, (*b*) calcite, and (*c*) dolomite.
7. Describe briefly the process used in the commercial production of lime.
8. What is the difference between quicklime and slaked lime?
9. Write equations for the reactions involved in the Solvay process (including provision for the production of sodium carbonate and recovery of ammonia).
10. Write equations for the reactions that occur in the formation of sodium carbonate by the LeBlanc process. Include an equation showing how this process could be used to produce sodium hydrogen carbonate.
11. What constitutes temporary and permanent hardness in natural waters?
12. By what methods may hardness be removed from natural waters?
13. Why is it desirable to soften natural waters?
14. Of the two compounds, $(NH_4)_2SO_4$ and $NaNO_3$, which would be better for use as a fertilizer if no difference in cost is assumed? Why?
15. Account for the fact that solutions of sodium phosphate are alkaline. Why should this behavior be expected?
16. Why is normal calcium phosphate not suitable for use as a fertilizer?

17. Write equations showing how the following compounds may be produced: (*a*) primary calcium phosphate, (*b*) calcium metaphosphate, (*c*) strontium pyrophosphate.

18. Assuming that the ore employed contains 60 per cent calcium phosphate, what weight of superphosphate fertilizer can be produced from 6 tons of the ore?

19. List one important use for each of the following substances: (*a*) KNO_3, (*b*) $NaHCO_3$, (*c*) NaCl, (*d*) CaO, (*e*) $Ca_3(PO_4)_2$, (*f*) $CaCO_3$, (*g*) $NaNO_3$, (*h*) $Ca(OH)_2$, (*i*) Na_2CO_3.

20. In what states are the following substances produced in quantity from natural deposits: (*a*) limestone, (*b*) sodium carbonate, (*c*) calcium phosphate?

21. In the processes studied in this chapter, cite cases in which provision is made for the recovery and use of by-products.

22. In converting normal calcium phosphate to the soluble primary salt, why is sulfuric acid used rather than phosphoric acid?

SUGGESTED READING

Journal of Chemical Education

HYLER, The Production of Salt, **12,** 203 (1935).

BRIGHTON, Salt-making on the Great Salt Lake, **9,** 407 (1932).

BLANK, Lime and Lime Kilns, **17,** 505 (1940).

CERNA, Industrial Water Conditioning Processes, **20,** 107, 191 (1943).

HOOVER, Water Purification and Water Softening at Columbus, Ohio, **4,** 945 (1927).

TURRENTINE, Synthetic Ammonia in the Fertilizer Industry, **6,** 894 (1929).

BEAUMONT, Concentrated Fertilizers: Problems for the Chemist and Agronomist, **6,** 899 (1929).

ALLISON, Nitrogen as a Plant Food, **3,** 51 (1926).

LIPMAN, The Nitrogen Problem in Agriculture, **4,** 845 (1927).

THOMPSON, Some Aspects of the Chemistry of Explosives, **20,** 151 (1943).

CAIRNS, Industrial and Military Explosives, **19,** 109 (1942).

GILLIE, Blasting Explosives, **5,** 1213 (1928).

WAGGAMAN, Phosphate Rock Industry of the United States, **10,** 391, 476 (1933).

RASK, An Introductory Story of Baking Powders, **9,** 1340 (1932).

VAIL, Sodium Silicates, Colloidal and Crystalline, **10,** 417 (1933).

Industrial and Engineering Chemistry

TIGER and SUSSMAN, Demineralizing Solutions by a Two-step Ion Exchange Process, **35,** 186 (1943).

MANSFIELD, Phosphate Deposits of the World, **34,** 9 (1942).

CHAPTER XXXIII

ORGANIC CHEMISTRY

I. HYDROCARBONS

In an earlier discussion of the broad aspects of the science of chemistry, attention was called to the fact that it is sometimes convenient to think of this vast body of knowledge in terms of rather arbitrary subdivisions (Sec. 1.1). The subject matter covered in the preceding chapters is concerned largely with limited aspects of inorganic chemistry together with many fundamental laws and principles which are usually thought of as falling within the scope of physical chemistry. In order that the student may have at least a very brief introduction to the subject, this and the succeeding three chapters will be devoted to the study of organic chemistry.

33.1. Historical

The term *organic* chemistry had its origin in the fact that early chemists were familiar with many compounds that were formed by or closely associated with living organisms. It was felt that these materials could be produced only through the agency of vital processes; hence the term. This viewpoint prevailed until the year 1828 when the German chemist, Wöhler (Fig. 142) made a discovery which was destined to have a profound influence upon the development of chemistry in general and organic chemistry in particular. Wöhler heated some ammonium cyanate (NH_4CNO) and found that it was thereby converted into urea [$CO(NH_2)_2$] a substance previously known only as a product of living organisms. Thus, from a purely inorganic

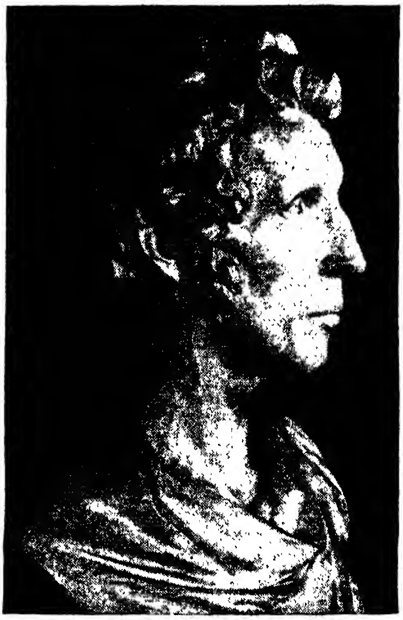


FIG. 142.—Friedrich Wöhler (1800–1882).

compound, Wöhler produced in the laboratory a typical organic compound and proved that vital processes are not a prerequisite to the formation of such substances.

Wöhler's discovery encouraged chemists to attempt the production, in the laboratory, of many other compounds previously obtained only from matter of animal or vegetable origin. That these efforts have met with truly remarkable success is reflected in the rapid growth of this phase of chemistry during the past hundred years. The chemist has not only succeeded in duplicating the substances arising from natural processes, but has produced many organic compounds which, so far as is known, are not formed by living organisms.

No one can say with certainty how many organic compounds are known. Estimates usually vary between 350,000 and 500,000. More accurate estimates are not possible since new organic compounds are being produced in chemical laboratories every day. In any event, the above estimates are impressive when one considers that the total of known inorganic compounds probably does not exceed 50,000.

It is also a striking fact that all organic compounds contain the element carbon. Consequently, chemists have discarded entirely the view that organic chemistry is restricted to substances of natural origin and now define this phase of chemistry as *the chemistry of the compounds of carbon.* In this multitude of compounds, the element carbon is found in chemical combination with hydrogen, oxygen, sulfur, nitrogen, phosphorus, and the halogens and, less frequently, with a few of the other elements. One is at once prompted to raise the question as to why one element (carbon) should participate in the formation of such a large number of compounds. In the following pages, attention will be directed toward a number of factors that will answer this question, at least in part.

33.2. Modes of Union of Carbon Atoms

The extensive development of organic chemistry has depended in great measure upon the chemist's ability to determine and represent the *structure* or architecture of organic molecules. This accomplishment is the result of an understanding of certain properties possessed in some measure by all kinds of atoms and in a unique degree by carbon. It will be recalled that the atomic number of carbon is six, the atomic weight is twelve, and that the structure of the carbon atom may be represented as shown in Fig. 143. For present purposes it is convenient to consider the carbon atom to be a tetrahedron in which the nucleus and the 2 electrons of the first shell are located within the body of the tetrahedron and the 4 "valence electrons" are situated at the

four corners. Since carbon most commonly enters into chemical union by sharing electrons, it follows that each carbon atom may form four covalent bonds each of which involves one shared pair of electrons. For example, in the compound CH_4, the carbon atom shares electrons with 4 hydrogen atoms.

Single Bonds. The unique character of the carbon atom centers largely upon its ability to share electrons *with other carbon atoms.* Thus, one may visualize two carbon atoms united, as shown in Fig. 144*a*. If, for convenience, *a straight line drawn between the two symbols is used to represent the shared pair of electrons*, the union of the 2 carbon atoms may be represented thus,

$$\cdot\underset{\cdot}{\dot{C}}-\underset{\cdot}{\dot{C}}\cdot$$

The line drawn between the two symbols is referred to as a *bond* and since only one pair of shared electrons is involved, this particular case is termed a *single bond.* In addition, each of these carbon atoms possesses additional electrons (represented by dots) which may be shared with other atoms, including other carbon atoms. Suppose, for example, that each of these 2 carbon atoms should unite with another carbon atom as shown below.

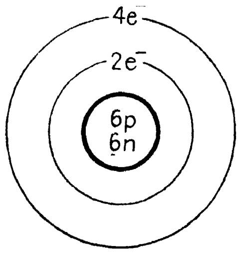


FIG. 143.—Diagram representing the structure of the carbon atom.

$$\cdot\underset{\cdot}{\dot{C}}-\underset{\cdot}{\dot{C}}-\underset{\cdot}{\dot{C}}-\underset{\cdot}{\dot{C}}\cdot$$

An extension of this process results in the formation of long chains of carbon atoms in which the carbon atoms are joined by single bonds.

Double Bonds. If two tetrahedral carbon atoms are joined by bringing together two edges so that two corners of each of the tetrahedra are in contact (Fig. 144*b*), the resulting union would involve a total of four shared electrons. This condition may be represented as follows:

$$\underset{\cdot}{\dot{C}}=\underset{\cdot}{\dot{C}}$$

and these carbon atoms are said to be joined by a *double bond.* Each carbon atom has two remaining electrons which may be used to establish additional bonds. Thus, each might be united with another carbon atom,

$$\cdot\dot{C}-\dot{C}=\dot{C}-\dot{C}\cdot$$

and, as suggested above, this process might be continued indefinitely to form longer and longer chains of carbon atoms involving both single and double bonds.

Triple Bonds. By bringing together one face of each of two tetrahedra, as shown in Fig. 144*c*, one may see how 2 carbon atoms may be joined by the sharing of electrons at each of three corners. In this

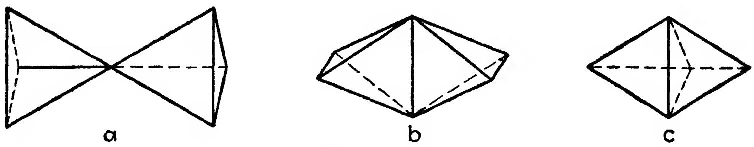


FIG. 144.—Illustration of modes of union of tetrahedral carbon atoms.

case the carbon-to-carbon union involves three shared pairs of electrons and this condition may be represented by

$$\cdot C \equiv C \cdot$$

Since each of these 2 carbon atoms has one remaining electron, it is possible to establish single bonds with other carbon atoms (or other kinds of atoms),

$$\cdot \dot{\underset{\cdot}{C}} - C \equiv C - \dot{\underset{\cdot}{C}} \cdot$$

and here again the possible extension of the length of the carbon chain is evident. It may also be seen that a variety of types of combination may be had depending on the number and position of double and/or triple bonds in the chain.

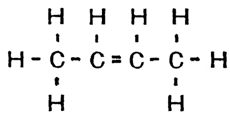
The ability of carbon atoms to unite with other carbon atoms by forming single, double, or triple bonds accounts in considerable measure for the large number of organic compounds. Other contributing factors will be noted in later sections of this chapter.

33.3. Types of Formulas

The simple formula and the true molecular formula for an organic compound may be established by essentially the same methods outlined in connection with the earlier discussion of formulas of inorganic compounds (review Sec. 3.4). Thus, one may determine that the simplest formula for an organic compound is C_2H_4, and that the true formula is C_6H_{12}. Although this information would be useful, it would be inadequate in most such cases because several different organic compounds might have this same molecular formula. In dealing with organic compounds, one usually must know not only the number of each kind of atom in the molecule but also the manner in

which they are arranged with respect to each other. In other words, it is usually required to know both the *composition* and the *structure* of the molecule.

In order to represent adequately the structure of organic molecules, use is made of *structural formulas.* Consider, for example, the molecular formula C_4H_8. Since more than one compound has this particular formula, a more revealing structural formula must be used to designate the particular compound in question, thus,



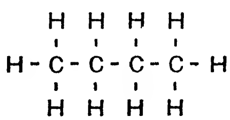
This formula not only shows clearly the arrangement of atoms in the molecule but also indicates the particular pair of carbon atoms joined by the double bond. Furthermore, since the bonds shown in the above formula represent shared pairs of electrons, it also may be seen from this formula that the valence of each carbon atom is four.

In order to save time, effort, and space, organic chemists have devised numerous ways of abbreviating these structural formulas. These devices might be described as semistructural formulas, but they need not be illustrated here. Until the student has become more familiar with the subject, it is considered best to write the complete structural formulas.

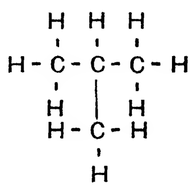
33.4. Isomerism

The existence of compounds (either organic or inorganic) that have the same molecular formula but different structures is known as *isomerism.* Two or more compounds which meet this requirement are said to be *isomers* or to be *isomeric.*

There are two structurally different compounds with the formula C_4H_{10}. The structural differences are shown by the following formulas:



and



It may be seen that one of these structures involves a straight and the other a branched chain of carbon atoms. As is true of all isomeric compounds, these two isomers have different chemical and physical properties, even though these differences may not be great.

There are several different types of isomerism, and no effort will be made here to discuss this subject in detail. It is worth while, however, to point out that isomerism may arise in different ways. For example, two or more isomers may exist because of the position of a double or triple bond, as shown by the following formulas:

$$\begin{array}{ccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & = & C & - & C & - & H \\ & & | & & & & & & | & & \\ & & H & & & & & & H & & \end{array} \quad \text{and} \quad \begin{array}{ccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & = & C & - & C & - & C & - & H \\ & & & & & & | & & | & & \\ & & & & & & H & & H & & \end{array}$$

The existence of isomeric compounds may be due to the position or mode of linkage of an element other than carbon. Such a case is illustrated by the following formulas:

$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array} \quad \text{and} \quad \begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

Numerous additional examples of isomerism will be encountered in the following discussions of different types of organic compounds. It will become increasingly evident that the phenomenon of isomerism contributes in considerable measure to the large number of known compounds of carbon.

33.5. Comparison of Organic and Inorganic Compounds

Before proceeding with the study of specific classes of organic compounds, it seems worth while to gain a general idea as to the comparative properties of organic and inorganic compounds. It should be clearly understood, however, that any attempts to generalize with respect to large numbers of chemical substances must involve many exceptions.

The most striking differences between organic and inorganic compounds arise from the fact that, *in general*, organic substances are predominantly covalent while inorganic materials are more likely to be predominantly ionic. From experience in the laboratory, the student should recall that many reactions involving the ions of inorganic compounds occur with extreme rapidity even at ordinary temperatures. On the other hand, the covalent organic substances react sluggishly at ordinary temperatures and in many cases only rather slowly at elevated temperatures. Although these behaviors are usually encountered, it is not difficult to cite numerous cases in which inorganic substances react slowly and organic compounds react rapidly.

In comparison with inorganic materials, the covalent character of

organic substances is reflected in their physical as well as their chemical properties. For example, most organic compounds are (*a*) nonelectrolytes, (*b*) relatively volatile, and (*c*) likely to be insoluble in water. In a general sense, just the reverse is most likely true of inorganic compounds. Similar broad generalizations may be made with respect to certain other physical properties.

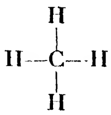
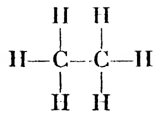
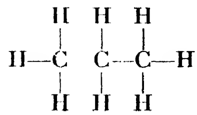
In connection with the phenomenon of isomerism, it is of interest to observe that up to the present time a *relatively* small number of cases of isomerism has been encountered among simple inorganic compounds. For this reason it is all too commonly assumed that the subject of isomerism is of importance only in relation to organic chemistry. As a matter of fact, the prevalence of different types of isomerism among complex inorganic compounds makes the study of isomerism an important phase of the subject of inorganic chemistry.

HYDROCARBONS

The hydrides of the element carbon are commonly known as *hydrocarbons*. In its ability to combine with hydrogen to form a wide variety of stable hydrides, carbon is truly a unique element. Were this not the case, one might expect a reasonable degree of similarity with regard to hydride formation by elements of the main family of Group IV. The unique character of carbon is amply illustrated by the fact that perhaps as many as 3000 hydrocarbons are known while the next element in the group (silicon) forms less than a dozen stable hydrides. Furthermore, the tendency toward hydride formation decreases regularly from silicon to lead. Fortunately, the hydrocarbons may be classified according to series, the members of which have many properties in common. Some attention will be devoted next to a study of a few of these large classes of hydrides of carbon.

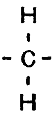
33.6. Paraffin Hydrocarbons

The simplest hydride of carbon in which all four of the valence electrons of the carbon atom are utilized in the formation of covalent bonds with hydrogen is that having the molecular formula, CH_4. This compound is known as *methane*, or sometimes as *marsh gas* since it is a product of the decay of organic matter in marshes. Methane is also the chief constituent of natural gas (Sec. 35.1). Commonly associated with methane in nature are other hydrocarbons which are chemically similar to methane and which together with methane are known as the *methane series* or *paraffin series* of hydrocarbons. The names, molecular formulas, and structural formulas of the first three members of this series are given in the accompanying table.

Name	Methane	Ethane	Propane
Molecular formula	CH_4	C_2H_6	C_3H_8
Structural formula			

An inspection of these structural formulas shows that these molecules are similar in that only single bonds are present. Hence, if these molecules are to enter into chemical reactions without rupturing the bonds between carbon atoms, they can react only by substitution of other atoms for hydrogen. Compounds of this type are said to be *saturated*, and this term is simply intended to imply that all the valence electrons are utilized in the formation of single bonds. In general, the chemical characteristics of this series of hydrocarbons are in accord with the name of the series, *i.e.*, *paraffin* hydrocarbons. The term *paraffin* is derived from the Latin, *parvum affinis* which means "little affinity." However, as will be shown later, this name should not be interpreted too literally.

Homologous Series. From the formulas CH_4, C_2H_6, and C_3H_8, it is evident that each succeeding member of this series differs from the preceding member by 1 carbon atom and 2 hydrogen atoms.



From this fact it follows that the molecular formula of the next member of the series (butane) should have the molecular formula C_4H_{10}; the next (pentane), C_5H_{12}, etc. These related hydrocarbons are said to constitute a *homologous series.* The general formula for this particular series is C_nH_{2n+2}.

In any homologous series, there is a more or less regular trend in physical properties in relation to molecular weight. Thus, in the methane series, the first four members are gases under ordinary atmospheric conditions, the next few members of the series are liquids, and those of still higher molecular weight are solids. As shown in Table 42, the boiling temperatures increase regularly with increase in molecular weight. It should be recognized, however, that the data in Table 42 refer only to the *straight-chain* compounds and do not include the boiling temperatures of isomers. It should also be noted

that all these hydrocarbons have names ending in *-ane* and that, beginning with the fifth member of the series, the prefix indicates the number of carbon atoms in the molecule.

Isomeric Saturated Hydrocarbons. Inspection of the structural formulas for methane, ethane, and propane shows that these formulas may not be rearranged in any manner that would lead to fundamentally different structures. From this it would be concluded that there are no isomeric forms of these compounds, and none has ever been found in nature or produced in the laboratory. In the case of butane (C_4H_{10}), however, one may write two different structural formulas (Sec. 33.4):

```
    H   H   H   H                        H   H   H
    |   |   |   |                        |   |   |
H - C - C - C - C - H      and       H - C - C - C - H
    |   |   |   |                        |   |   |
    H   H   H   H                        H   |   H
                                           H-C-H
                                             |
                                             H
```

It is significant that only these two isomers would be predicated on the basis of possible structural formulas and that two and only two isomeric butanes are known. Since both of these compounds are *butanes*, different names must be used for them. In every case, the straight-chain isomer is called the *normal* isomer and the name is usually written as *n*-butane. The branched chain butane is known as *isobutane*.

If one should continue to use structural formulas as a basis for the

TABLE 42
BOILING TEMPERATURES OF SOME SATURATED HYDROCARBONS

Formula	Name	Boiling temperature, °C. at 760 mm.
CH_4	Methane	−164.0
C_2H_6	Ethane	− 86.0
C_3H_8	Propane	− 38.5
C_4H_{10}	Butane	1.0
C_5H_{12}	Pentane	37.0
C_6H_{14}	Hexane	69.5
C_7H_{16}	Heptane	98.4
C_8H_{18}	Octane	125.5
C_9H_{20}	Nonane	149.7
$C_{10}H_{22}$	Decane	173.0
$C_{11}H_{24}$	Undecane	194.5
$C_{12}H_{26}$	Dodecane	214.5
$C_{13}H_{28}$	Tridecane	234.0

TABLE 43

THE NUMBER OF ISOMERS OF CERTAIN PARAFFIN HYDROCARBONS*

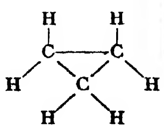
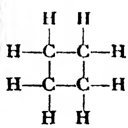
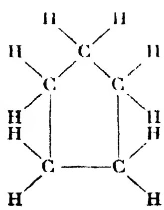
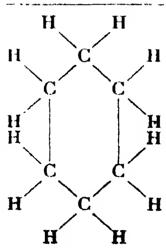
Molecular Formula	Number of Isomers
CH_4	0
C_2H_6	0
C_3H_8	0
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{11}H_{24}$	159
$C_{12}H_{26}$	355
$C_{13}H_{28}$	802
$C_{14}H_{30}$	1858
$C_{18}H_{38}$	60,523

* HENZE and BLAIR, *Journal of the American Chemical Society*, 53, 3077 (1931).

prediction of the number of isomers, it would be predicted that there should be three pentanes, five hexanes, and nine heptanes. With increase in the number of carbon atoms, the possibilities for different structural arrangements increase with great rapidity, as is shown in Table 43. Although it is true that many of the isomers of hydrocarbons of higher molecular weight have never been produced in the laboratory or found in nature, it is also true that no one has ever succeeded in producing more isomers than would be predicted from structural formulas. The extent to which isomerism contributes to the large number of known and possible organic compounds should be clearly evident from the data of Table 43.

33.7. Cyclic Saturated Hydrocarbons

In addition to saturated hydrocarbons having structures that involve open chains (either straight or branched) of carbon atoms, there is the added possibility of structures in which the carbon atoms are arranged in closed-chain or ring structures. Such compounds are well known and are usually referred to as *cyclic* saturated hydrocarbons. The names and formulas of the four most common compounds of this type are given in the accompanying tabulation.

Name...............	Cyclopropane	Cyclobutane	Cyclopentane	Cyclohexane
Molecular formula....	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}
Structural formula....				

The general formula for this series is C_nH_{2n}. These compounds are similar to those of the methane series in that they are saturated compounds and thus may react only by substitution unless the reactions are such that carbon-to-carbon linkages are broken. The cyclic compounds differ from those of the paraffin series in that their chemical behaviors are not so closely related as one might expect of the members of a homologous series. Whereas *n*-butane and *n*-pentane are quite similar in their chemical behavior, cyclobutane and cyclopentane exhibit marked differences in chemical properties.

Although this series includes members beyond cyclohexane, relatively little is known about the cyclic saturated hydrocarbons involving rings of more than 6 carbon atoms.

From an inspection of the structural formulas of members of this series, it is evident that there can be only one cyclobutane, one cyclopentane, etc.

33.8. Unsaturated Hydrocarbons

Compounds that contain atoms joined by double or triple bonds are said to be *unsaturated*. Although there are many hydrocarbons that fall in this category, only a few of them will be considered here.

Because of the presence of double or triple bonds (*i.e.*, unsaturation) these compounds can react by direct union or addition. Thus, ethylene which contains a double bond may unite directly with hydrogen to form ethane,

$$\begin{array}{ccc} H & & H \\ & \diagdown \quad \diagup & \\ & C = C & \\ & \diagup \quad \diagdown & \\ H & & H \end{array} + H_2 \rightarrow \begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

and acetylene which contains a triple bond may combine with hydrogen also to form ethane,

$$H-C\equiv C-H + 2H_2 \rightarrow \begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

This type of reaction serves to distinguish between saturated and unsaturated hydrocarbons since the latter react only by substitution. In general, although unsaturated hydrocarbons react preferentially by addition, under suitable conditions they may be caused to react by substitution and not by addition.

Ethylene. This compound is the first member of a homologous series of the general formula C_nH_{2n} and sometimes is called the *ethylene*

series. The various members of this series exhibit similar chemical properties although, as is usually the case, the first member of the series possesses some chemical properties not shared by other members of the series.

Ethylene is one of a number of unsaturated hydrocarbons produced during the "cracking" of petroleum (Sec. 36.1). This compound may be produced readily in the laboratory by the catalytic dehydration of ethyl alcohol.

$$C_2H_6O \rightarrow \begin{array}{ccc} H & & H \\ & \diagdown\;\;\diagup & \\ & C=C & \\ & \diagup\;\;\diagdown & \\ H & & H \end{array} + H_2O$$

Most of the reactions of ethylene and related hydrocarbons depend upon the presence of the double bond. By addition, these substances react with hydrogen, the halogens, ozone, hypochlorous acid, etc., to form products that are useful as such or in the production of still other organic substances.

Ethylene is used, with oxygen, as an anesthetic. It is also used to promote the ripening of citrus fruits. No less important is the fact that ethylene serves as a raw material for the commercial or laboratory-scale production of a wide variety of other organic compounds. Mustard gas is produced by the reaction between ethylene and sulfur monochloride.

$$2 \begin{array}{ccc} H & & H \\ & \diagdown\;\;\diagup & \\ & C=C & \\ & \diagup\;\;\diagdown & \\ H & & H \end{array} + S_2Cl_2 \rightarrow \begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ Cl & - & C & - & C & - & S - C & - & C & - & Cl \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array} + S^{\circ}$$

Acetylene. The first member of the homologous series of hydrocarbons containing one triple bond and having the general formula C_nH_{2n-2} is acetylene (C_2H_2). Despite the fact that the compounds of this series contain triple bonds, their addition reactions occur somewhat less readily than do those of the ethylene series. The chemical properties of the members of the acetylene series are generally similar and, since it is by far the most important compound of its series, acetylene is the only compound that will be considered here.

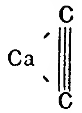
Acetylene may be produced by the hydrolysis of calcium carbide (Sec. 29.7), by subjecting other hydrocarbons to the action of an electric discharge, and by the catalytic decomposition of methane at elevated temperatures.

$$2\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H} \rightarrow \mathrm{H{-}C{\equiv}C{-}H} + 3\mathrm{H_2}$$

Aside from its addition reactions, acetylene is of interest chemically for the reason that it behaves as a weak acid, and it may be considered to ionize as follows:

$$H_2C_2 \rightleftharpoons H^+ + (HC_2)^-$$
$$(HC_2)^- \rightleftharpoons H^+ + (C_2)^-$$

Accordingly, acetylene should be expected to react with strong bases to form either acid or normal salts, and both types are well known. The acetylides of sodium and calcium are typical.

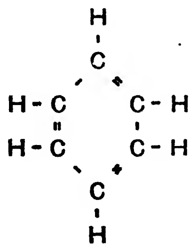
$NaC{\equiv}CH$ 

The fact that calcium carbide is completely hydrolyzed (Sec. 28.7) is wholly in harmony with facts presented previously (Sec. 19.2).

Acetylene is used as a fuel in oxyacetylene torches and as a raw material for the production of certain varieties of synthetic rubber. Many useful organic compounds may be made from acetylene, acetic acid being one with which the student is already familiar.

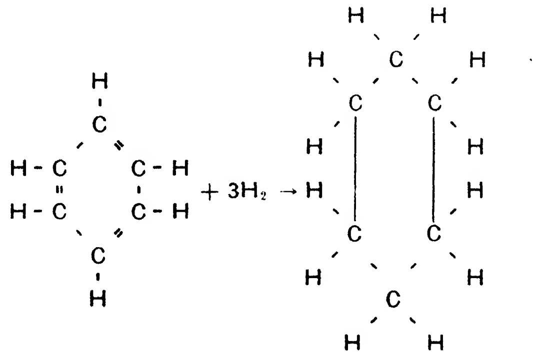
Benzene. Of a wide variety of cyclic unsaturated hydrocarbons containing six or less carbon atoms per molecule, only the compound known as *benzene* and having the molecular formula C_6H_6 will be considered here. The choice of benzene for the purposes of the present discussion centers largely about the fact that this compound is unusual among organic compounds in the extent to which it is looked upon as a "parent substance." In other words, a large number of common and useful organic materials may be thought of as related to, or derived from, benzene.

The question as to how best to represent the structure of the benzene molecule is one that has occupied the attention of many chemists. For most purposes, the structure of this compound may be represented in the manner first suggested by Kekule and shown in detail as follows:



According to this structural formula, the benzene molecule is represented as a hexagonal arrangement of 6 carbon atoms, each of which is joined to 1 hydrogen atom. In order to preserve the idea of the almost invariable tetravalence of the carbon atom and at the same time represent a structure that is in harmony with the chemical nature of benzene, it is necessary to show also in this structure a total of three double bonds.

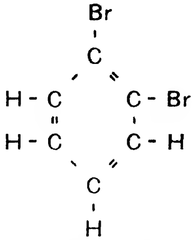
It is feasible here only to summarize briefly the chief chemical characteristics of benzene. This substance is much less reactive than would be expected in view of the fact that the molecule contains three double bonds. Although benzene does participate in addition reactions, it does so much less readily than compounds such as ethylene. For example, benzene reacts with hydrogen to form cyclohexane.

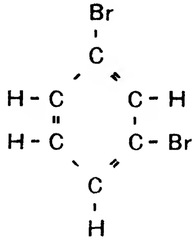


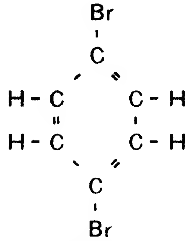
In general, benzene reacts more readily by substitution. In these reactions, other atoms or groups of atoms (radicals, or "groups") are substituted for the hydrogen atoms in the benzene molecule. The resulting compounds are often referred to as *substitution products* or *derivatives* of benzene.

If the atom or group substituted for hydrogen may be represented by X and if only 1 hydrogen atom is displaced by X, it might appear that six isomers having the formula C_6H_5X might be anticipated. It is found, however, that only one such compound can be formed, *e.g.*, there is only one compound having the formula, C_6H_5Br. From this fact it follows that, so far as this particular substitution reaction is concerned, the same product is formed no matter which of the 6 hydrogen atoms is replaced. If, on the other hand, two or more hydrogen atoms are displaced, isomerism is possible and is realized. Thus, there are three isomeric compounds of the type $C_6H_4X_2$. If X is a bromine atom, there are three dibromobenzenes ($C_6H_4Br_2$) and the

three isomers may be designated by use of the prefixes *ortho-*, *meta-*, and *para-*, as shown below:

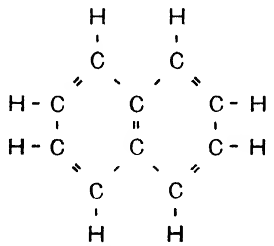

ortho-Dibromobenzene

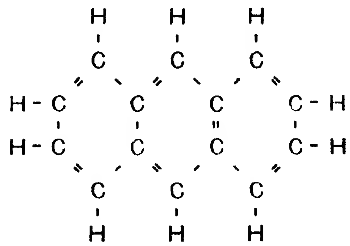

meta-Dibromobenzene


para-Dibromobenzene

The nature of X may be varied widely. In the next chapter, a number of the more common substitution products, or derivatives, of benzene will be studied and, in this connection, it will be evident that suitable choice of the substituent atom or group (X) gives rise to an almost unlimited number of different organic compounds.

Cyclic Unsaturated Hydrocarbons of Higher Molecular Weight. Only for the purpose of calling attention to organic compounds having structures involving more than one ring of carbon atoms, there are given below structural formulas for napthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$):


Naphthalene


Anthracene

Like benzene, these compounds react more readily by substitution than by addition. It requires no great measure of imagination for the student to realize that a very large number of derivatives of these compounds are possible. With the added fact that there are many other similar but still more complicated organic compounds, the student should begin to gain some appreciation of the complexities of structural organic chemistry. As far as the following discussions are concerned, these somewhat more complex organic compounds will be considered only to the extent that they must be mentioned in connection with their occurrence in nature or with their relation to common and useful materials produced in the laboratory.

33.9. Hydrocarbon Radicals

Before proceeding with the study of some additional types of organic compounds, it will be helpful to recognize that, just as certain groups of atoms in inorganic compounds may be termed *radicals*, a similar designation may be useful in the study of organic chemistry. It should be kept in mind, however, that, because of the predominantly covalent character of organic compounds, organic radicals are less likely to enjoy a relatively independent existence than is the case among ionic inorganic compounds.

If a compound is formed by substitution of some other atom for one of the hydrogen atoms of methane, only a part of the molecule is involved in the change,

$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array} \qquad \begin{array}{ccc} & H & \\ & | & \\ H- & C & - \\ & | & \\ & H & \end{array}$$

and that which remains of the original molecule of methane may be called a *radical* since it went through the indicated reaction apparently unchanged. In organic chemistry, it is more common practice to refer to these radicals as *groups*. Thus, the radical derived from methane is called a *methyl* group. Similarly, the radical formed by removing 1 hydrogen atom from ethane is called an *ethyl group*, etc. The name of the radical is formed from the name of the parent hydrocarbon by substituting *-yl* for *-ane*. In the case of the cyclic hydrocarbon benzene, the corresponding radical is the *phenyl* group, $C_6H_5^-$.

Attention will be called to other organic radicals in following discussions. No effort will be made here to consider radicals formed by removal of more than 1 hydrogen atom, unsaturated radicals of the ethylene or acetylene series, or the question of nomenclature of radicals related to the various isomeric forms of saturated hydrocarbons.

EXERCISES

1. Particularly in relation to fundamental laws and theories studied earlier, list several important similarities between organic and inorganic compounds.

2. What are the chief differences between inorganic and organic compounds?

3. Give several examples of inorganic compounds which are predominantly covalent.

4. Define the following terms (*a*) organic chemistry, (*b*) isomerism, (*c*) double bond, (*d*) structural formula, (*e*) hydrocarbon, (*f*) unsaturated compound, (*g*) homologous series, (*h*) hydrocarbon radical or group.

5. Suggest a chemical method whereby one might distinguish between ethane and ethylene.

6. Write structural formulas for all of the isomers of *n*-pentane and *n*-hexane.

7. If most organic compounds are covalent, should they be expected to behave as electrolytes or nonelectrolytes? Why?

8. What one property of the element carbon is largely responsible for its ability to form so many different compounds?

9. Write structural formulas for (*a*) *n*-butane, (*b*) benzene, (*c*) acetylene, (*d*) carbonic acid.

10. In a structural formula, what is the significance of a straight line drawn between two symbols?

11. In the acetylene series, what would be the molecular formula of the hydrocarbon containing 18 carbon atoms?

12. By means of equations employing structural formulas, show how acetylene may be successively converted to ethylene and ethane.

SUGGESTED READING

Journal of Chemical Education

WILLIAMS, Ionization and the Atomic Structure Theory in Organic Chemistry, **4,** 867 (1927).

CHRISTIAN, Calculation of Numbers of Isomeric Paraffins, **11,** 51 (1934).

BAILAR, The Study of (Inorganic) Isomerism in Courses in General Chemistry, **8,** 310 (1931).

ARENTZ, Uses of Ethylene, **2,** 459 (1925).

Industrial and Engineering Chemistry

MCARDLE and ROBERTSON, Solvent Properties of Isomeric Paraffins, **34,** 1005 (1942).

CHAPTER XXXIV

ORGANIC CHEMISTRY

II. DERIVATIVES OF THE HYDROCARBONS

In order to render somewhat less arduous the task of correlating a considerable number of different types of organic compounds, it is helpful to look upon these types as being related to the saturated or unsaturated hydrocarbons. These relationships may be either direct or indirect and need not be practical from the standpoint of actual chemical transformations suitable for use in the laboratory. Suppose, for example, that a compound B may be produced from a hydrocarbon A, and that B in turn may be converted to another compound C.

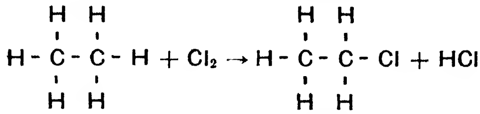
$$A \rightarrow B \rightarrow C$$

Although it may not be possible to produce C directly from the hydrocarbon A, it may be convenient to consider C as having been derived from A. Such genetic relationships are particularly useful for purposes of classification.

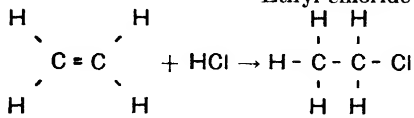
When it is desired to produce some specific organic compound, it is not uncommonly necessary to start with whatever materials may be available and successively produce several intermediate compounds. By this rather indirect approach, there may be formed a substance from which the desired compound may be produced. Frequently, the starting material may be a hydrocarbon or a simple derivative of a hydrocarbon. In the following discussion of a few different classes of organic compounds, an effort will be made to show the manner in which the various compounds are related to relatively simple hydrocarbons.

34.1. Organic Halogen Compounds

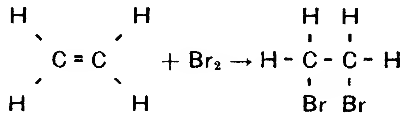
Halogen compounds may be produced directly from either saturated or unsaturated hydrocarbons. Thus, ethyl chloride which is used as a local anesthetic may be produced from ethane by a substitution reaction or from ethylene by addition.



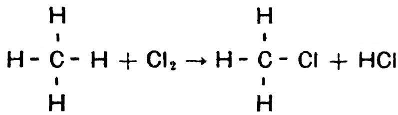
Ethyl chloride



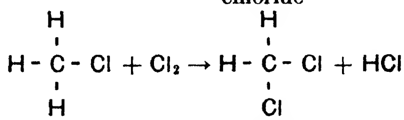
Ethylene dibromide (which is used in conjunction with lead tetraethyl in the production of gasoline having a high antiknock rating) may be formed most conveniently by the addition of bromine to ethylene.



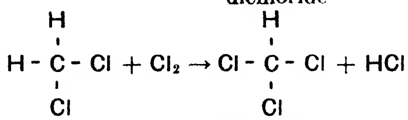
The formation of organic halogen compounds is by no means restricted to the replacement of only 1 or 2 atoms of hydrogen. By exercising suitable control over the conditions under which the reactions occur, it is possible to produce several different halogen compounds from a single simple hydrocarbon. Thus, from the reaction between methane and chlorine, four different chlorine derivatives of methane may be produced.



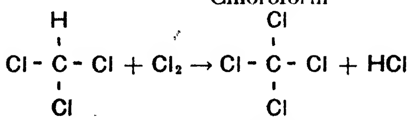
Methyl chloride



Methylene dichloride



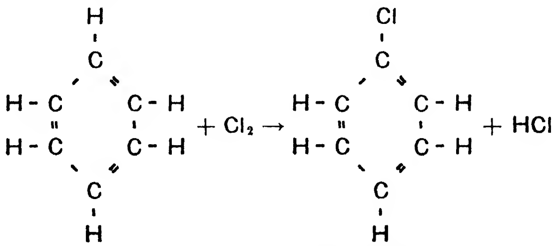
Chloroform



Carbon tetrachloride

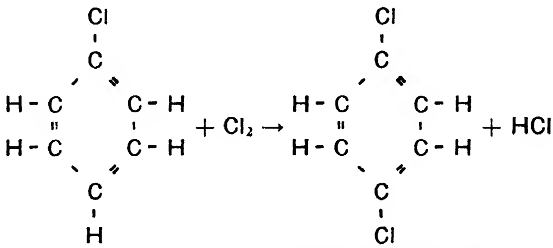
Mixed halogen derivatives are also possible, and some of them are common and useful substances. For example, dichlorodifluoromethane (CCl_2F_2) is known commercially as *Freon* and in recent years has come to be widely used as a refrigerant in place of ammonia or sulfur dioxide.

Halogen compounds may be formed readily from hydrocarbons such as benzene by substitution. The introduction of 1 atom of chlorine produces chlorobenzene,



Chlorobenzene
(or phenyl chloride)

while the introduction of a second atom of chlorine produces the three isomeric (*ortho-*, *meta-*, and *para-*) dichlorobenzenes. Paradichlorobenzene is commonly used as an insecticide, particularly to combat moths. The formation of this compound from chlorobenzene is shown by the following equation:



*para-*Dichlorobenzene

All the foregoing examples of organic halogen compounds illustrate their relationship to the corresponding hydrocarbons. These examples have been restricted to more or less direct formation from hydrocarbons or their simple derivatives. There are many less direct means whereby organic halogen compounds may be produced, but these methods need not be considered here.

34.2. Alcohols and Phenols

Organic compounds known as *alcohols* and *phenols* are characterized by the fact that these compounds have structures involving one or

more —OH groups attached to carbon. Thus the characteristic structural group is

$$\begin{array}{c} | \\ -\mathrm{C}-\mathrm{OH} \\ | \end{array}$$

The structural formulas of the two simplest alcohols are given below

$$\begin{array}{cc} \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H}-\mathrm{C}-\mathrm{OH} \\ | \\ \mathrm{H} \end{array} & \begin{array}{c} \mathrm{H}\quad\mathrm{H} \\ |\quad\;\; | \\ \mathrm{H}-\mathrm{C}-\mathrm{C}-\mathrm{OH} \\ |\quad\;\; | \\ \mathrm{H}\quad\mathrm{H} \end{array} \\ \text{Methyl alcohol} & \text{Ethyl alcohol} \\ \text{(wood alcohol)} & \text{(grain alcohol)} \end{array}$$

From the above formulas it may be seen that these alcohols are related to the hydrocarbons methane and ethane, respectively, in the sense that in each case an —OH group has been substituted for a hydrogen atom of the parent hydrocarbon.

It is sometimes both instructive and useful to look upon the alcohols and phenols as being structurally related to water (HOH). Each of the above alcohols, for example, may be thought of as a compound in which a hydrocarbon radical is substituted for one of the hydrogen atoms of a water molecule.

Methyl Alcohol. Methyl alcohol, which is also known as *methanol*, is one of several organic materials produced by the dry distillation of hardwoods (Sec. 35.4), hence the common name *wood alcohol*. Most of the methanol produced commercially at the present time is formed by a catalyzed reaction between carbon monoxide and hydrogen (Sec. 36.3).

$$\mathrm{CO} + 2\mathrm{H_2} \rightarrow \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H}-\mathrm{C}-\mathrm{OH} \\ | \\ \mathrm{H} \end{array}$$

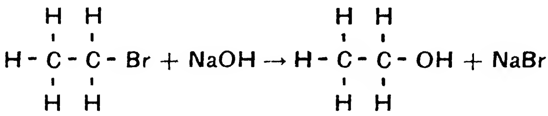
A more general method of preparation (*i.e.*, one that may be used to produce, in the laboratory, a variety of simple alcohols) involves treatment of the appropriate organic halogen compound with a strong base such as sodium hydroxide.

$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H}-\mathrm{C}-\mathrm{Cl} \\ | \\ \mathrm{H} \end{array} + \mathrm{NaOH} \rightarrow \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H}-\mathrm{C}-\mathrm{OH} \\ | \\ \mathrm{H} \end{array} + \mathrm{NaCl}$$

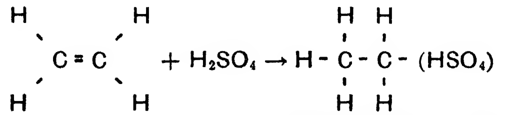
Methyl alcohol is a liquid under ordinary atmospheric conditions. In both the liquid and gaseous forms it is very poisonous, causing

blindness, insanity, and death. This alcohol is an excellent solvent for fats, oils, resins, and other organic substances.

Ethyl Alcohol. The alcohol that is the active ingredient of alcoholic beverages is known as *ethyl alcohol*, *ethanol*, or by the common name *grain alcohol*. Aside from its common method of formation by alcoholic fermentation, ethyl alcohol may be produced in a variety of ways. The general method cited above may be used by employing, for example, ethyl bromide.

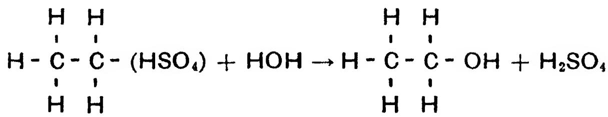


Another method involves the formation of ethyl hydrogen sulfate by the reaction between ethylene and sulfuric acid,



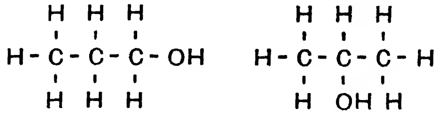
Ethyl hydrogen sulfate

followed by hydrolysis,



Industrial alcohol is a product that contains 95 to 96 per cent of C_2H_6O, the remainder being water. It is this particular product that is usually known as *grain alcohol*. After suitable treatment to remove all but a few tenths of 1 per cent of water, the commercial product is known as *absolute alcohol*. In addition to its uses as products of the fermentation industries, most of the laboratory and industrial uses for this compound depend upon the fact that ethyl alcohol is an excellent solvent. Large quantities of ethanol are used in the production of lacquers, medicinals, explosives, synthetic rubber, dyes, and a wide variety of other organic substances.

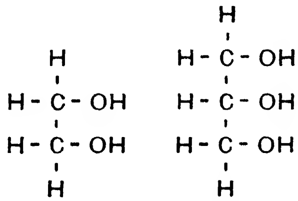
Isomeric Simple Alcohols. An inspection of the structural formulas for methyl and ethyl alcohols suggests that isomeric alcohols should not be expected and none are known. However, two structural formulas may be written for the simple alcohol which is structurally related to the saturated hydrocarbon propane, and two isomers are known. The structural formulas and names of these alcohols are



n-Propyl alcohol *iso*-Propyl alcohol

Because *n*-propyl alcohol contains an —OH group attached to a carbon atom which is in turn bound to only one other carbon atom, this alcohol is classified as a *primary* alcohol. Since the carbon atom bearing the —OH group in *iso*-propyl alcohol is attached to two other carbon atoms, this alcohol is said to be a *secondary* alcohol. The importance of this distinction will become evident in connection with later discussions of other types of organic compounds which may be produced from primary and secondary alcohols.

Other Alcohols. In addition to simple alcohols related to saturated hydrocarbons containing more than 3 carbon atoms, attention should be called to alcohols containing in their structures more than one —OH group. Two relatively simple and common alcohols in this category are ethylene glycol and glycerol (*glycerine*). Ethylene glycol is used chiefly in the manufacture of explosives and as an antifreeze liquid in automobile radiators.[1] Glycerol is employed in the manufacture of explosives, as a moistening agent in cigarettes, and in the production of resins and a wide variety of other organic products.



Ethylene glycol Glycerol

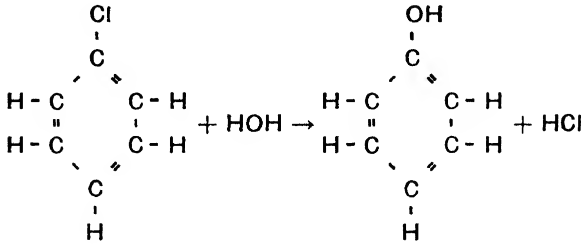
From these formulas, it may be seen that ethylene glycol and glycerol are structurally related to ethane and propane, respectively.

There are many known alcohols containing two or more —OH groups. Carbohydrates, such as the common sugars and starches, may be classified as alcohols in the sense that these molecules contain several —OH groups. A few compounds of this type will be mentioned more specifically in a later chapter.

Phenols. Compounds which are derived from benzene and which contain one or more —OH groups attached to the carbon atoms of the benzene ring are referred to broadly as phenols. Specifically, the name *phenol* is applied to the compound having the formula C_6H_5OH, which

[1] Ethylene glycol for this use is sold under various trade names, *e.g.*, Prestone.

is commonly known as *carbolic acid.* There are many ways in which phenols may be produced; *e.g.*, phenol is produced as shown by the equation,



This reaction must be carried out at elevated temperatures in the presence of a catalyst. Other phenols may be produced in a similar manner or by less direct methods.

In addition to its familiar use as a germicide, phenol is employed commercially in a number of different ways. Large quantities of this material are used in the manufacture of synthetic resins of the type exemplified by Bakelite. Phenol is particularly useful as a starting material for the production of other organic compounds which are useful as dyes, medicinals, explosives, etc. Thus phenol may be converted readily to picric acid, which is the chief constituent of the explosive known as *lyddite.*

Acidic Properties of Alcohols and Phenols. On the basis of their structural relationship to water, it might be concluded that alcohols and phenols are analogous to inorganic bases such as sodium hydroxide. If the hydrocarbon group of the alcohol or phenol is represented by R, the structural comparison may be shown by the formulas,

$$\mathrm{Na-O-H} \qquad \mathrm{H-O-H} \qquad \mathrm{R-O-H}$$

In view of this rather obvious relationship, it is somewhat surprising to learn that alcohols actually behave as very weak acids, while phenols have still more pronounced acidic properties. Phenol itself is an acid sufficiently strong to change the colors of certain indicators. Alcohols and phenols behave as bases only in the presence of stronger acids.

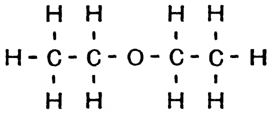
34.3. Ethers

Organic molecules that contain the structural arrangement

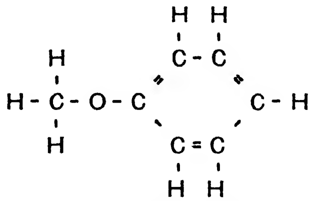
$$-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{C}}}-$$

are known as *ethers.* The three remaining bonds of each of the two

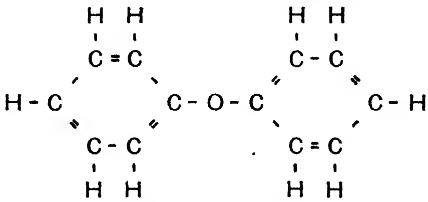
carbon atoms may be attached to hydrogen atoms, other carbon atoms, etc. The structural formulas for some typical ethers are given below.



Diethyl ether



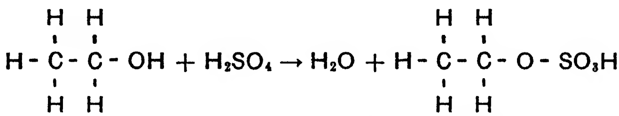
Methyl phenyl ether



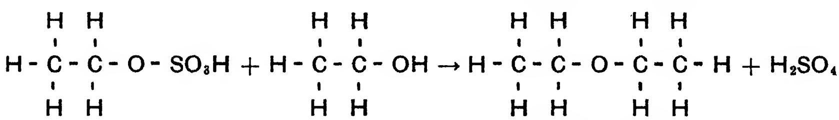
Diphenyl ether

From these formulas it may be seen that the two organic groups attached to oxygen may be the same or different. It is also evident that ethers are named in terms of the names of the corresponding organic radicals. From the standpoint of structural relationships, diethyl ether, for example, may be looked upon as a substitution product of water (*i.e.*, an oxide) or as a compound formed by substitution of 1 oxygen atom for 2 hydrogen atoms, one from each of 2 molecules of ethane.

The most common ether, and the one to which the general term *ether* is often specifically applied, is diethyl ether. This compound is readily prepared by the reaction between ethyl alcohol and concentrated sulfuric acid.



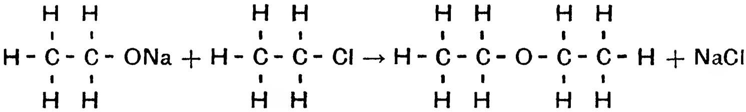
Ethyl sulfuric acid



Diethyl ether

It is of interest to note that, in the presence of the relatively strong acid, sulfuric, the very weak acid, ethyl alcohol, behaves as a base.

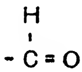
Diethyl ether may be produced also by a reaction that serves as a general method for the preparation of a wide variety of ethers.



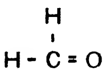
Diethyl ether is a colorless volatile liquid boiling at 35°C., *i.e.*, just a little above ordinary room temperature. This is the ether so commonly used as a general anesthetic. Diethyl ether is also used extensively as a solvent for oils, fats, waxes, resins, and other organic materials.

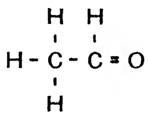
34.4. Aldehydes

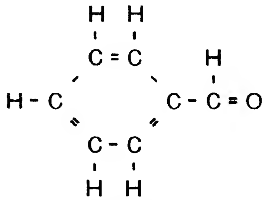
The products formed by subjecting primary alcohols to the action of mild oxidizing agents are known as *aldehydes.* The structural unit that characterizes the aldehydes is



Thus, carbon is bound to oxygen by a double bond (which does not have the characteristics of a double bond between 2 carbon atoms), to hydrogen, and by the remaining bond to hydrogen or to another carbon atom. The structural formulas for three common aldehydes are given below.







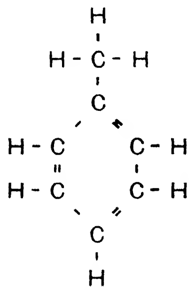
Formaldehyde Acetaldehyde Benzaldehyde

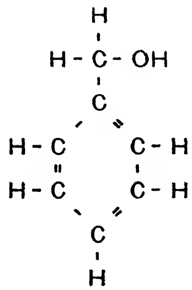
Formaldehyde, acetaldehyde, and benzaldehyde are structurally related to, and may be considered to be derivatives of, methane, ethane, and benzene, respectively.

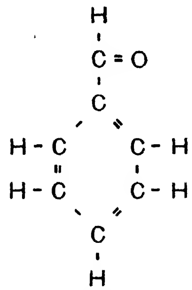
Formaldehyde is produced on a large scale by the oxidation of methyl alcohol with the oxygen of the atmosphere at high temperatures and in the presence of a copper catalyst. The formaldehyde of commerce is most commonly sold as a 40 per cent aqueous solution, known as *formalin.* Some formaldehyde is produced in the form of a white solid which is known as *paraformaldehyde* and which may be repre-

sented by the formula $(CH_2O)_n$. This is simply a convenient means of indicating that paraformaldehyde consists of an association of many molecules (where n is a large number) of formaldehyde and that the exact value of n is not known or is variable. The chief use for formaldehyde is in the production of resinous products of the type exemplified by Bakelite. This aldehyde is also used in the compounding of embalming fluids, in the manufacture of other organic chemicals, and as a germicide and disinfectant. The practice of producing gaseous formaldehyde by burning paraformaldehyde "candles" in closed rooms in dwellings and elsewhere is on the decline because the disinfectant or germicidal properties of formaldehyde vapor are not so pronounced as formerly believed.

Benzaldehyde (oil of bitter almonds) may be produced by the oxidation of the primary alcohol known as *benzyl alcohol* which, in turn, is derived from methyl benzene or toluene. These relationships are shown schematically below


Methyl benzene (toluene)


Benzyl alcohol


Benzaldehyde

Much benzaldehyde is used in the manufacture of dyes. Relatively smaller quantities are employed in the production of perfumes and certain artificial flavors.

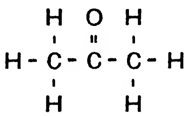
Many common sugars contain aldehyde groups in addition to —OH groups (Sec. 34.2).

34.5. Ketones

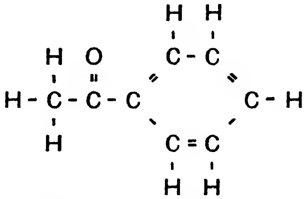
The action of mild oxidizing agents upon *secondary* alcohols results in the formation of a class of compounds known as *ketones*. All ketones contain the characteristic *carbonyl group.*

$$-\overset{\displaystyle O}{\overset{\|}{C}}-$$

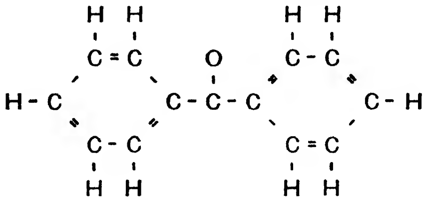
This may be seen by an inspection of the following structural formulas of three typical ketones:



Dimethyl ketone
(acetone)



Methyl phenyl ketone
(acetophenone)



Diphenyl ketone
(benzophenone)

It will be noted that the carbonyl group is similar to the aldehyde group and, from this fact, it might be inferred that aldehydes and ketones should exhibit similar chemical properties. Although this is true in considerable degree, a detailed study of these two types of compounds reveals a number of important differences.

Acetone is the most important ketone and is the only substance of this type that will be considered here. In accordance with the method of formation suggested above, acetone may be prepared by the oxidation of the secondary alcohol, isopropyl alcohol. Together with calcium carbonate, acetone is formed by heating dry calcium acetate. In recent years, there have been devised several methods for the commercial production of acetone and, in general, these methods involve complex changes that are beyond the scope of the present discussion. Most of the important uses for acetone depend upon the fact that this liquid is an excellent solvent. As such, it is useful in the production of resins, plastics, lacquers, paint and varnish removers, etc. A number of important organic chemicals including chloroform are produced from acetone.

Attention has already been called to the fact that the molecules of many carbohydrates contain both alcohol and aldehyde groups. These substances may also contain carbonyl groups; hence in some measure such carbohydrates are to be classed as ketones. It should become increasingly evident to the student that some of the more com-

plex organic molecules may contain the particular groups that are characteristic of different types of organic compounds. That such is the case is an important contributing factor in accounting for the large number of known and possible organic compounds.

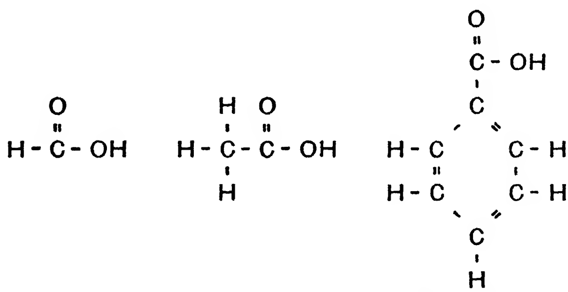
34.6. Organic Acids

Just as primary alcohols are converted to aldehydes by the action of mild oxidizing agents, so the aldehydes are converted to organic acids when treated with somewhat stronger oxidizing agents.

$$\text{Primary alcohol} \xrightarrow{\substack{\text{mild}\\ \text{oxidizing}\\ \text{agent}}} \text{aldehyde} \xrightarrow{\substack{\text{stronger}\\ \text{oxidizing}\\ \text{agent}}} \text{organic acid}$$

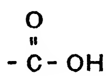
If a primary alcohol is treated directly with a relatively strong oxidizing agent, the product obtained is the corresponding acid; however, the aldehyde is probably formed as an intermediate.

The acids corresponding to formaldehyde, acetaldehyde, and benzaldehyde may be represented by the structural formulas given below.



Formic acid Acetic acid Benzoic acid

The group of atoms characteristic of the organic acids is



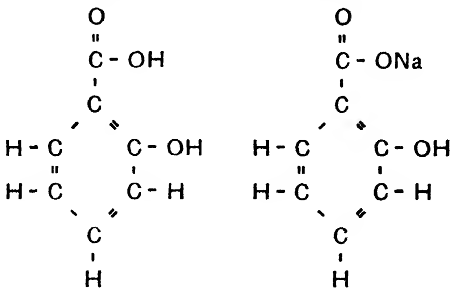
which is commonly known as the *carboxyl* group.

Formic acid is the simplest possible organic acid and, since it contains only 1 carbon atom per molecule, is related to the saturated hydrocarbon, methane. Because this acid may be obtained from the bodies of red ants, it was given the name *formic* (from the Latin word

formica, meaning ant). There are many suitable laboratory methods for the production of formic acid or its salts, but these need not be considered here. In general, its properties are somewhat different from those of other more typical organic acids.

Acetic acid is formed by the oxidation of acetaldehyde and is genetically related to ethane. Heretofore the formula for acetic acid has been written $HC_2H_3O_2$ in order to emphasize the fact that this acid molecule contains only one ionizable hydrogen. From the structural formula given above, it is evident that the hydrogen in question must be that which is present in the carboxyl group and which is attached to oxygen rather than to carbon. The student is already familiar with the fact that acetic acid is a relatively weak acid. Concentrated acetic acid contains very little water and is known as *glacial* acetic acid. Among other commercial methods, the concentrated acid is obtained as one of several products formed by the dry distillation of wood (Sec. 35.4). Vinegar is essentially a dilute solution of acetic acid (4 to 5 per cent by volume) in water. Vinegars produced from fruit juices are known as *cider* vinegars and usually possess a characteristic aroma of the fruit from which the vinegars are produced. The so-called *spirit* vinegars are made from pure acetic acid (from natural or synthetic sources) and are usually colorless although a brownish-yellow color may be imparted by the addition of caramel. In addition to its use in the manufacture of vinegar, large quantities of acetic acid are used in the production of rayon, plastics, solvents, flavoring essences, etc. The quantities of acetic acid used as a laboratory reagent are by no means unimportant.

Benzoic acid is a white crystalline solid which is only sparingly soluble in water. This acid is found in cranberries and numerous other naturally occurring materials. Benzoic acid is related to benzene since the molecule may be looked upon as one in which a carboxyl group has been substituted for one of the hydrogen atoms of the benzene molecule. The sodium salt of benzoic acid (sodium benzoate) is commonly employed as a preservative for food and medicinal preparations. In addition to benzoic acid, there are many important and useful organic substances which are related to this acid in the sense that their molecules contain substituent groups in addition to the carboxyl group. For example, salicylic acid consists of molecules in which a hydroxyl group is substituted for the hydrogen atom on a carbon atom adjacent to that to which the carboxyl group is attached. The sodium salt of this acid has long been used as a medicinal in the treatment of arthritis. The structural formulas of the parent acid and the sodium salt are given below.



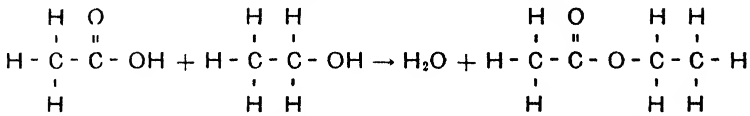
Salicylic acid Sodium salicylate

By comparison with inorganic acids, such as hydrochloric or sulfuric, the typical organic acids are to be classified as relatively weak acids. Although there are some notable exceptions, organic acids are generally very slightly ionized in their aqueous solutions. Thus it appears that the chemical bond between hydrogen and oxygen (in the carboxyl group) is predominantly covalent rather than ionic. In conformity with the fact that organic acids exhibit only weakly acidic properties, the salts of these acids are usually extensively hydrolyzed.

34.7. Esters

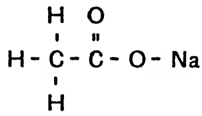
The reaction that occurs when an alcohol and an acid are brought together under suitable conditions may be understood best by comparison with a type of reaction with which the student is already familiar. Consider, for example, the reaction between hydrochloric acid and sodium hydroxide and that between acetic acid and ethyl alcohol.

$$\underset{\text{Acid}}{H^+Cl^-} + \underset{\text{Base}}{Na^+OH^-} \rightarrow \underset{\text{Water}}{H_2O} + \underset{\text{Salt}}{Na^+Cl^-}$$



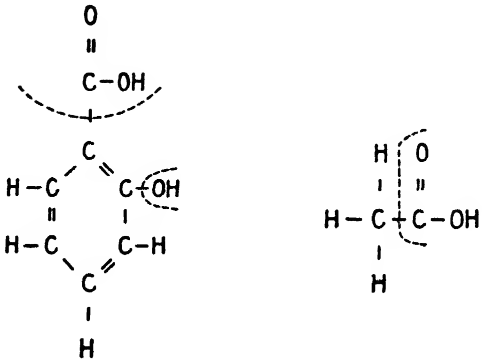
Acid Alcohol Water Ester (ethyl acetate)

From these equations the reaction between an organic acid and an alcohol appears to be analogous to that between an acid and a base. It is seen also that organic esters are analogous to salts as far as their apparent mode of formation is concerned. The ester represented above is known as *ethyl acetate*, a name that appears to be wholly appropriate when one compares the structural formula of ethyl acetate with that of the salt, sodium acetate.

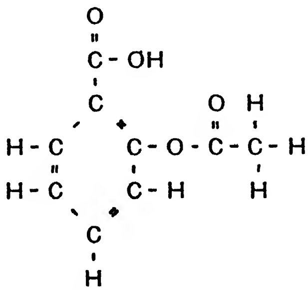


Ethyl acetate is an excellent solvent, and large quantities of this material are used in the production of lacquers, varnishes, and a wide variety of other useful products.

In order to pursue still further the mode of formation of esters, consider the possibility of reaction between salicylic acid and acetic acid.



Of the three potentially acidic groups (set off by dotted lines), one must assume a basic role if the formation of an ester is to occur. Since the phenolic —OH group in the salicylic acid molecule is the most feebly acidic of the three and since the carboxyl group in the acetic acid molecule is the most strongly acidic group of the three, the formation of an ester must depend upon their interaction. The resultant ester, acetyl salicylic acid, is commonly known as *aspirin*.



Acetyl salicylic acid
(aspirin)

Additional examples of esters common in everyday life might be cited. Perhaps it is sufficient here to call attention to the fact that

esters are widely used in the compounding of artificial flavors, perfumes, etc. A list of esters and the natural flavors that they simulate are given in Table 44.

TABLE 44

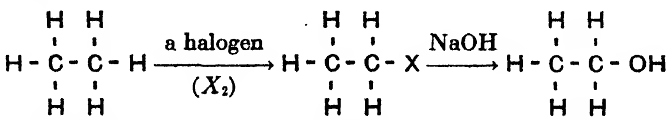
ESTERS USED AS ARTIFICIAL FLAVORS

Name of Ester	Natural Flavor
Isobutyl formate	Raspberry
Isobutyl acetate	Raspberry
Amyl acetate	Banana
Isoamyl acetate	Pear
Octyl acetate	Orange
Methyl butyrate	Pineapple
Butyl butyrate	Pineapple
Amyl butyrate	Apricot
Isoamyl isovalerate	Apple

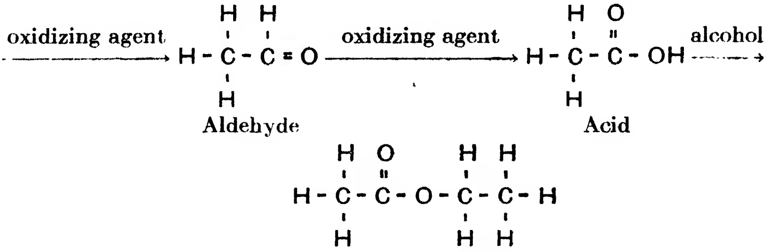
Ethyl butyrate, ethyl nonylate, and amyl undecylate all simulate the odors of the rose and are employed in the preparation of perfumes, toilet waters, etc. Methyl salicylate (the methyl ester of salicylic acid) is the chief component of oil of wintergreen and is employed in the production of medicinals, perfumes, and flavors. Additional examples of esters and their uses will be encountered in the following chapters.

34.8. Genetic Relationships

The manner in which much of the subject matter of organic chemistry may be correlated in terms of types of compound has been emphasized repeatedly. Numerous attempts have also been made to demonstrate that it is profitable to look upon many of these types as derivatives of the hydrocarbons. Finally, it has been suggested that, in order to produce a given type of compound, it may be necessary to start with whatever material may be available and arrive at the desired product only after having produced one or more intermediate types. Given below is a *schematic* representation of some of these relationships. Structural formulas are given only for the types that it is desired to emphasize; the nature of other essential reactants is indicated above the arrows which indicate the sequence of chemical conversions.



Hydrocarbon — Organic halogen compound — Alcohol

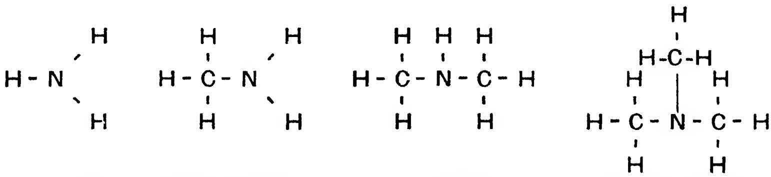


Aldehyde Acid Ester

In addition it should be recalled that, an alcohol having been produced, this product may be used in the preparation of an ether, or in the preparation of a ketone in the case of a secondary alcohol. The hydrocarbon ethane is used only as an example.

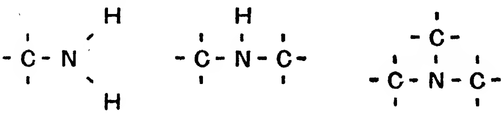
34.9. Amines

Before proceeding to the study of certain other aspects of the subject of organic chemistry, it is necessary to consider still an additional class of compounds, *viz.* the *amines*. These substances are structurally related to ammonia in the same sense that alcohols and ethers are related to water, *i.e.*, the amines may be considered as being derived from ammonia by substitution of one or more hydrocarbon radicals for one or more of the hydrogen atoms of the ammonia molecule. The structural formulas given below are typical examples.



Ammonia Methylamine Dimethylamine Trimethylamine

In accordance with the number of radicals substituted for hydrogen, the amines are known as *primary*, *secondary*, and *tertiary*. Thus, methylamine is a primary amine, dimethylamine is a secondary, and trimethylamine a tertiary amine. The groupings of atoms characteristic of these three types are given below.

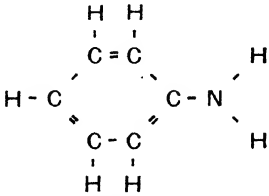


Primary Secondary Tertiary

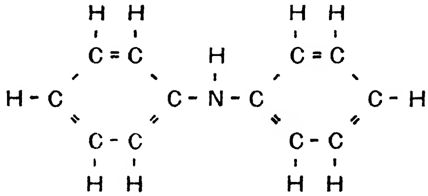
Disregarding the attached carbon atoms, the group (—NH_2), (=NH), and (≡N) are known as the *amino*, *imino*, and *nitrilo* groups, respectively.

As will become evident from discussions which are to follow, amines occur in abundance and great variety in nature. The production of many different individual amines in the laboratory may be accomplished by a variety of methods.

The three methylamines mentioned above are illustrative only of the simplest amines. By suitable choice of the substituent groups, one may produce ethylamines, propylamines, butylamines, etc. One also may prepare simple (or complex) amines containing different substituent groups, *e.g.*, ethyl methylamine, dimethyl propylamine, etc. The simple amines are characterized by a fishlike odor. Among other relatively simple amines may be included compounds such as aniline and diphenylamine, which are of great importance in the manufacture of dyes, medicinals, etc.



Aniline
(phenylamine)



Diphenylamine

It is of interest to note that aniline, for example, may be looked upon as derived from either ammonia or benzene. If one were particularly interested in the hydrocarbon part of the molecule, one would consider aniline as a compound in which an amino group is substituted for one of the hydrogen atoms of the benzene molecule. These structural relationships so often emphasized in the study of organic chemistry are more than mere formal relationships that are convenient for purposes of classification. The amines, for example, are related to ammonia both structurally and in terms of chemical properties. Thus, ammonia is a basic compound, and the amines also are basic in a degree that is related to the number and nature of the substituent groups. Similarly, just as ammonia reacts with water and with the hydrogen halides,

$$NH_3 + HOH \rightleftharpoons (NH_4)OH$$
$$NH_3 + HBr \rightleftharpoons (NH_4)Br$$

so the amines behave similarly as shown by the following equations in which hydrocarbon radicals are represented by R in order to emphasize generality.

$$R_3N + HOH \rightleftharpoons (NHR_3)OH$$
$$R_2N-H + HBr \rightleftharpoons (NH_2R_2)Br$$

Further information concerning specific amines will be acquired through the study of the following chapters.

EXERCISES

1. Organic halogen compounds are usually considered as substitution products of the corresponding hydrocarbons. Cite one type of reaction involving an organic halogen compound which suggests that these compounds might be looked upon as substitution products of, for example, hydrogen chloride.

2. What grouping of atoms is characteristic of each of the following types of organic compounds: (*a*) ethers, (*b*) primary amines, (*c*) aldehydes, (*d*) secondary alcohols?

3. Write complete structural formulas to illustrate (*a*) a ketone, (*b*) an ester, (*c*) a tertiary amine, (*d*) an organic acid. In each case, write the name of the compound used as the example.

4. Point out one or more important differences between (*a*) absolute alcohol and grain alcohol, (*b*) a primary alcohol and a secondary alcohol, (*c*) an alcohol and a phenol.

5. Justify the statement that glycerol is both a primary and a secondary alcohol.

6. Write structural formulas for (*a*) *n*-butyl phenyl ether, (*b*) propionaldehyde, (*c*) *meta*-dipropylbenzene, (*d*) ethyl isopropyl ketone, (*e*) methyl butyrate, (*f*) dimethyl propyl amine.

7. Listed below are the names of some common commercial products. Identify each in terms of the specific organic compound (or compounds) involved: (*a*) formalin, (*b*) *Prestone*, (*c*) aspirin, (*d*) *Freon*, (*e*) *Bakelite*, (*f*) carbolic acid.

8. What volume of chlorine gas (at 25°C. and 752 mm.) would be required to convert 38 g. of methane to chloroform if a 46 per cent yield is assumed?

9. Cite one important use for each of the following compounds: (*a*) acetone, (*b*) ethylene dibromide, (*c*) phenol, (*d*) ethyl acetate, (*e*) carbon tetrachloride, (*f*) methyl alcohol, (*g*) formaldehyde, (*h*) aniline.

10. What weight of by-product hydrogen chloride would be produced during the production of 1 lb. of *p*-dichlorobenzene from benzene if it is assumed that the ortho and para isomers are formed in the ratio of 1 to 4?

11. Starting with the appropriate hydrocarbon in each case, write equations showing how one could produce each of the following compounds: (*a*) butyric acid, (*b*) propionaldehyde, (*c*) di-*n*-propyl ether.

12. Justify the view that (*a*) the —OH group in certain organic molecules possesses amphoteric properties, (*b*) esters are analogous to salts, (*c*) ethers may be regarded as oxides.

SUGGESTED READING

Journal of Chemical Education

Green, Lamprey, and Sommer, Properties vs. Performance of Present Day Anti-freeze Solutions, **18,** 488 (1941).

Bogert, Recent Progress in the Field of Synthetic Perfumes, **8,** 1311 (1931).

Industrial and Engineering Chemistry

McBee, Hass, Neher, and Strickland, Chlorination of Methane, **34,** 296 (1942).

Guillanden, Glycerol, **29,** 729 (1937).

Cooley, Acetone, **29,** 1399 (1937).

CHAPTER XXXV

ORGANIC CHEMISTRY

III. ORGANIC MATERIALS OF NATURAL ORIGIN

In the two preceding chapters the student has been faced with a seemingly endless array of different types of organic compounds. As a matter of fact, the few types considered thus far represent only a mere beginning.

It has been implied that there are many suitable methods whereby all these different compounds may be produced in the laboratory, and only casual reference has been made to their existence in nature. In the present chapter, attention will be directed toward a few of the more important natural sources of organic materials.

35.1. Natural Gas

The chief organic compound obtained from natural gas is the saturated hydrocarbon, *methane.* Small quantities of other volatile hydrocarbons (*e.g.*, ethane and propane) and occasionally small quantities of nitrogen, carbon dioxide, and helium are associated with the methane. Although the composition is quite variable, the average methane content is about 80 per cent by volume and may be as low as a few per cent or as high as 95 per cent.

Although most of the natural gas produced is used as a fuel, it is of interest to note the manner in which appropriate chemical treatment of methane may lead to the production of other useful compounds. Thus, methane may be converted to methyl chloride from which methyl alcohol may be produced. The methyl alcohol in turn may be used in the production of formaldehyde, formic acid, esters, etc. In this, as in many other cases that will be discussed in the following pages, a natural supply of one or more raw materials makes possible the chemical production of many other useful forms of matter.

35.2. Petroleum

The drilling of the first oil well in Titusville, Pa., in 1859, marked the beginning of the modern petroleum industry which has developed into one of the most fruitful sources of organic chemicals. From wells which may vary in depth from a few feet to more than 2 miles, there is

obtained a dark-colored liquid known as *crude petroleum* or *crude oil.* This material has a characteristic odor, and its composition varies considerably in relation to the locality in which it is found. The annual production of crude petroleum amounts to approximately 2 billion barrels, considerably more than one-half of which is produced in the United States. The most important domestic production areas are found in the state of Texas, which supplies about 40 per cent of the crude petroleum produced annually in the United States. The combined production of Oklahoma and California is about equal to that of Texas, while less important areas are found in Louisiana, Kansas, New Mexico, Pennsylvania, Michigan, Arkansas, and Wyoming.

The products obtainable from crude petroleum are known commonly by names such as *gasoline, kerosene, lubricating oils, paraffin, vaseline,* and *asphalt.* All these common products consist of very complex mixtures of hydrocarbons. It is therefore necessary to consider the means by which they may be separated from each other and then to consider the problems involved in obtaining pure chemicals from the various mixtures.

Refining of Crude Petroleum. The hydrocarbons in petroleum range in composition from butane (C_4H_{10}) to high-molecular-weight compounds containing as many as 40 carbon atoms per molecule. When heat is supplied to such a mixture, the more volatile components of low molecular weight vaporize first. As the temperature of the mixture is progressively increased, the less volatile components are volatilized. Thus, by a process of *fractional distillation* crude petroleum may be separated into a number of fractions each of which boils over a more or less definite range of temperatures and contains hydrocarbons falling within a fairly definite range of molecular weights. From these statements it should not be inferred that the fractions obtained represent sharp separations. With respect to the individual components, there is considerable overlapping, *i.e.*, two fractions may contain varying percentages of the same constituent.

In Table 45 are listed a number of fractions that may be obtained by the fractional distillation of petroleum, together with the temperature ranges over which these fractions boil at atmospheric pressure, and an *estimate* of the range of molecular formulas of the hydrocarbons present in each fraction. It should be clearly understood that the fractions specified do not necessarily represent those separated in any particular refinery.

Once the crude petroleum is separated into these gross fractions, each fraction may then be subjected to further refining. Ordinarily, the various fractions are treated with sulfuric acid primarily for the

purpose of removing objectionable unsaturated hydrocarbons. After separation of the acid, the petroleum products are washed with sodium hydroxide solution which neutralizes the last traces of acid and serves to remove certain alkali-soluble sulfur compounds. Thereafter, the various fractions are not infrequently subjected to redistillation conducted for the purpose of accomplishing further fractionation.

TABLE 45

PRODUCTS OF THE FRACTIONAL DISTILLATION OF CRUDE PETROLEUM

Common name	Boiling range, °C.	Constituent hydrocarbons (approximate)
Casinghead gasoline	35–70	C_4H_{10} to C_6H_{14}
Gasoline (light to medium)	70–100	C_6H_{14} to C_7H_{16}
Gasoline (medium to heavy)	100–215	C_8H_{18} to $C_{12}H_{26}$
Kerosene	150–300	C_9H_{20} to $C_{18}H_{38}$
Gas oil	>300	$C_{12}H_{26}$ to $C_{20}H_{42}$
Lubricating oils	>300	$>C_{20}H_{42}$
Petroleum jelly	>300	$>C_{20}H_{42}$
Paraffin	>300	$>C_{20}H_{42}$

There remains, of course, the question as to whether crude petroleum or the various fractions obtained therefrom may serve as a source of *pure* hydrocarbons. Because the fractions listed in Table 45 are extremely complex mixtures of hydrocarbons with similar physical and chemical properties, the problem of resolving such mixtures into their component compounds is difficult indeed. Nevertheless, much progress in this direction has been made in recent years, largely as a result of improved methods of distillation.

35.3. Coal

In an earlier discussion it was pointed out that coke is produced by heating bituminous coal in the presence of a limited supply of oxygen. Since the metallurgical industries require large quantities of coke, the coal is commonly heated under conditions favorable to the production of the maximum quantity of coke from a given weight of coal. On the other hand, if one is interested primarily in the other products obtainable from coal, somewhat different conditions may be employed in order to produce relatively less coke and more of the desired products.

The products obtained from the dry distillation of coal fall into four groups: (*a*) coal gas, an important fuel consisting principally of hydrogen, methane, carbon monoxide, and nitrogen, (*b*) coke, (*c*) coal tar, (*d*) ammonia. The relative quantities of these various products

formed are dependent upon the grade of coal employed, the temperature, the rate of application of heat, and other factors. As an approximation, it may be stated that 1 ton of coal may be expected to yield 10,000 cu. ft. of coal gas, 1500 lb. of coke, 150 lb. of coal tar, and about 5 lb. of ammonia. Hereafter, emphasis will be placed upon the coal-tar fraction since it is from this material that many useful organic substances are obtained.

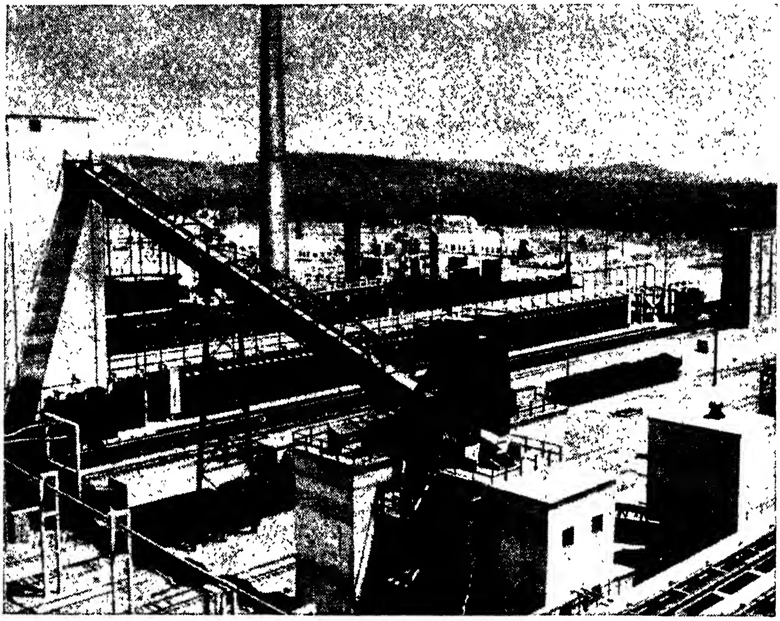


FIG. 145.—A battery of modern by-product coke ovens located at the plant of the Lone Star Steel Company, Daingerfield, Tex. (*Courtesy of Koppers Company, Inc.*)

Chemicals from Coal Tar. By a process of fractional distillation, crude coal tar may be separated into fractions designated as light, middle, and heavy oils. The light oil is composed of materials that boil at temperatures below 190°C. and consists largely of benzene together with smaller amounts of toluene and the xylenes. The middle oils boil between 190° and 230°C. and contain phenol (carbolic acid), cresols (the ortho, meta, and para methylphenols), naphthalene, and small amounts of numerous other substances. The quantity of phenol and cresols usually present amounts to about 2 per cent of the original coal tar. Because these products are weak acids, they may be extracted by treating the oil with dilute sodium hydroxide solution. The phenols and cresols react to form water-soluble sodium salts. After separation of the resulting water solution from the water-insolu-

ble (and alkali-insoluble) oils, the phenols and cresols are regenerated by acidification and separated by fractional distillation.

The heavy oils are obtained at distillation temperatures above 230°C. This fraction contains substituted phenols and cresols having molecular weights greater than those found in the middle oil fraction. Another important product obtained from the heavy oils is the hydrocarbon anthracene.

It is an interesting fact that, until a few years ago, coal tar was considered an undesirable by-product and was almost entirely wasted. After it was learned that so many valuable organic compounds could be obtained from coal tar, the ovens used in the production of illuminating gas and coke were designed in a manner that permits the collection and utilization of the coal-tar oils. Some idea of the magnitude of these industrial operations may be gained from Fig. 145 and from the fact that about half a billion gallons of coal tar are produced annually in the United States alone. Chemicals from coal tar serve as the raw materials for the production of an almost endless list of useful materials including explosives, medicinals, perfumes, dyes, and plastics.

35.4. Wood

As a source of organic compounds, wood is relatively less important than either crude petroleum or coal. Furthermore, the use of wood as a source of organic chemicals such as acetic acid, methyl alcohol, and acetone is far less important than it was a few decades ago. The nature of the organic materials obtained by the dry distillation (sometimes called *destructive distillation*) of wood depends primarily upon the variety of wood employed.

Resinous Wood. If the gum exuded by the pine tree when it is "bled" or "boxed" is distilled with steam, there is obtained a product known as *turpentine*, a complex mixture of oils. *Wood turpentine* is the name given to the product obtained by the steam distillation of resinous pine stumps left behind in lumbering operations. The principal constituent of turpentine is a complex unsaturated hydrocarbon having a ring structure, the molecular formula $C_{10}H_{16}$, and the name *pinene.* Other related hydrocarbons are also present in crude turpentine but their separation is difficult. When crude turpentine is distilled with steam, there remains a residue known as *rosin* or *colophony.* This material is not a true resin, but it is sometimes used as such in the manufacture of varnishes. When rosin is subjected to further dry distillation, it yields a distillate known as *rosin oil.* This material is used in the manufacture of laundry soaps, axle grease, and as an unsatisfactory substitute for linseed oil in paints.

Nonresinous Wood. The destructive distillation of nonresinous wood, such as that of the beech tree, yields the following products: (*a*) an aqueous distillate known as *pyroligneous acid.* This material contains about 1 per cent of methyl alcohol, 6 to 8 per cent of acetic acid, and small quantities of acetone. Thus, three important organic chemicals are made available. (*b*) A distillate known as *wood tar.* There is very little use for this material and it is used chiefly as a fuel. (*c*) A

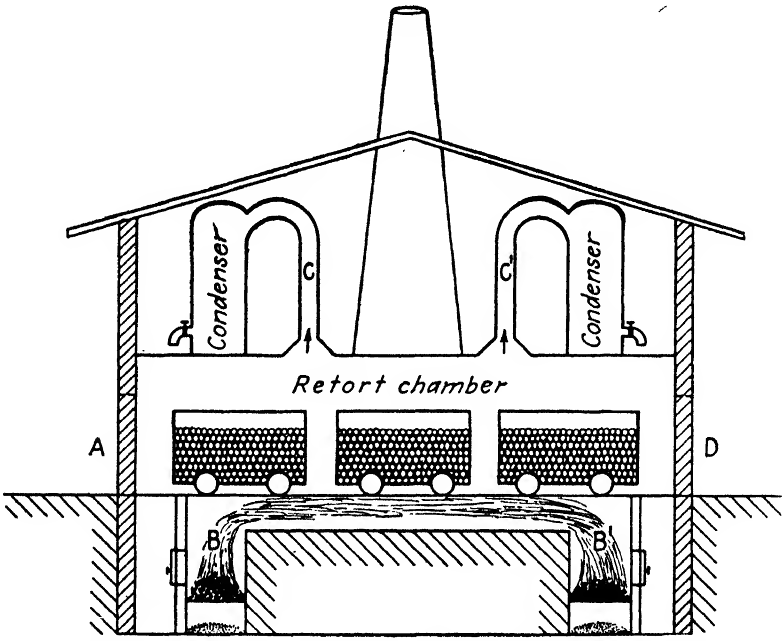
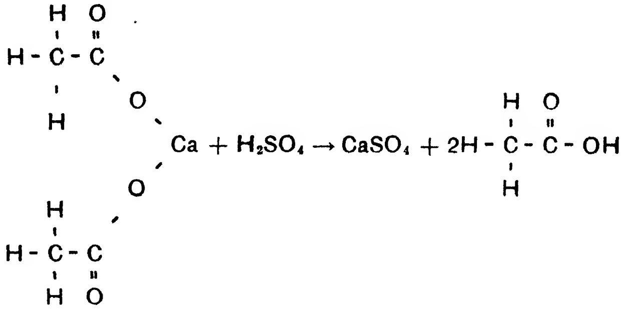


FIG. 146.—The destructive distillation of wood. Iron cars loaded with wood enter the retort chamber through a door at *A*, heat is supplied by the fireboxes *B* and *B'* for a period of about twenty-four hours, and the volatile products leave the chamber through pipes *C* and *C'*, and enter the condensers. *Pyroligneous acid* is drained from the condensers, and the more volatile products are permitted to escape. The residual charcoal remaining in the iron cars is removed through a door, *D*.

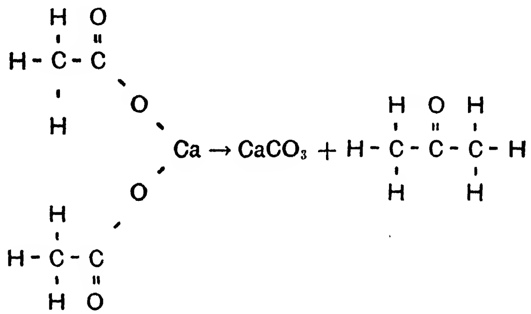
solid residue of wood charcoal. This is the chief product for which wood is destructively distilled, and the other materials are to be looked upon as by-products. The properties and uses of wood charcoal have been considered in an earlier discussion (Sec. 28.3).

The destructive distillation of nonresinous wood is carried out as shown in Fig. 146. The pyroligneous acid is separated from traces of wood tar, neutralized by treatment with lime, and fractionally distilled to separate the methyl alcohol. The remainder is evaporated to dry-

ness to obtain calcium acetate. From this product, pure acetic acid may be obtained by heating the salt with sulfuric acid.



The acetic acid is distilled from the reaction mixture and the nonvolatile calcium sulfate remains. If, on the other hand, the dry calcium acetate is heated to its decomposition temperature, acetone is produced.



Thus, in addition to the acetone produced directly, additional acetone may be formed from the acetic acid by the intermediate production of calcium acetate.

35.5. Animal and Vegetable Fats and Oils

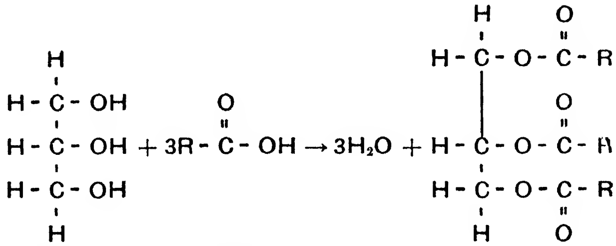
Although somewhat limited with regard to the variety of organic materials involved, fats and oils of animal and vegetable origin are nevertheless important sources of organic compounds. Common examples of naturally occurring materials that fall within this category include lard, beef tallow, butter, olive oil, linseed oil, cottonseed oil, corn oil, castor oil, and tung oil. All the fats and oils of this type are glyceryl esters of typical organic acids.

It will be recalled that glycerol is an alcohol containing three —OH groups. Each of these groups is capable of reacting with the carboxyl group of an organic acid to form a typical ester linkage (Sec. 34.7).

Since the organic acids obtainable from animal and vegetable fats and oils are mostly ones of high molecular weight and therefore contain long chains of carbon atoms, it will be convenient in the present discussion to represent the hydrocarbon part of these acid molecules by the letter R, thus,

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

If one wished to form a fat or oil in the laboratory, this could be accomplished by the reaction between 1 mole of glycerol and 3 moles of the appropriate organic acid.



Glycerol Organic acid Ester (fat or oil)

The physical and chemical properties of the fat or oil depend primarily upon the nature of the organic acid employed. If the hydrocarbon part of the acid contains one or more double or triple bonds, the corresponding oil will be a liquid under ordinary conditions of temperature. If, on the other hand, the hydrocarbon radical of the parent acid is saturated, the glyceryl ester is usually a white solid. Information relating to the hydrocarbon portion of several organic acids to be obtained from fats or oils is given in Table 46.

TABLE 46

ORGANIC ACIDS RELATED TO FATS AND OILS

Name of acid	*R*	Nature of unsaturation
Butyric	C_3H_7-	None
Lauric	$C_{11}H_{23}-$	None
Palmitic	$C_{15}H_{31}-$	None
Stearic	$C_{17}H_{35}-$	None
Oleic	$C_{17}H_{33}-$	One double bond
Linoleic	$C_{17}H_{31}-$	Two double bonds
Linolenic	$C_{17}H_{29}-$	Three double bonds
Isolinolenic	$C_{17}H_{29}-$	One double bond and one triple bond

Among the most common fats and oils are the glyceryl esters of palmitic, stearic, oleic, and linoleic acids. The names and melting temperatures of these esters are given in Table 47.

TABLE 47
Glyceryl Esters of Organic Acids

Name of acid	Name of ester		Melting temperature of ester, °C.
	Common	Systematic	
Palmitic	Palmitin	Glyceryl palmitate	60
Stearic	Stearin	Glyceryl stearate	71
Oleic	Olein	Glyceryl oleate	17
Linoleic	Linolein	Glyceryl linoleate	0

As they are obtained from natural sources, fats and oils usually consist of rather complex mixtures of glyceryl esters. If one wishes to extract a pure ester from a naturally occurring fat or oil, it is necessary to subject it to a suitable refining process. The approximate composition of a number of common fats and oils is given in Table 48.

TABLE 48
Approximate Composition of Some Common Fats and Oils

Fat or oil	Composition, %		
	Stearin and palmitin	Olein	Linolein
Beef tallow	70–75	20–25	0
Butter*	50–55	40–45	0
Cottonseed oil	20–25	20–25	45–50
Olive oil	20–25	65–70	5–10
Linseed oil†	7–10	15–20	30–35

* Butter also contains glyceryl butyrate.
† In addition, linseed oil contains 40 to 45 per cent of other esters of glycerol.

The many available fats and oils serve as sources of pure esters of glycerol. However, the chief uses for these fats and oils employ mixtures which have been subjected to only limited refining. Fats and oils are used extensively as foods, in the manufacture of paints, and as the raw materials for the production of numerous other useful substances, some of which will be discussed in the following paragraphs and in Chap. XXXVI.

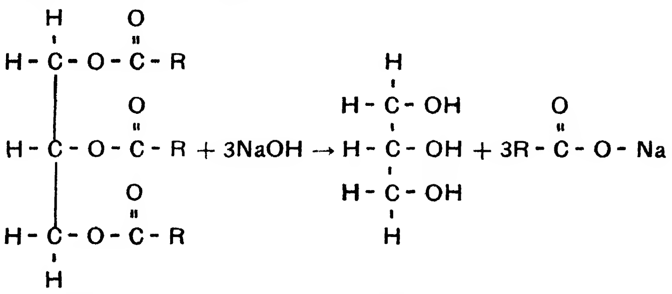
Hydrolysis of Fats and Oils. From the preceding discussion it should be evident that, in addition to serving as sources of glyceryl

esters, animal and vegetable fats and oils are potential sources of glycerol and many organic acids. The manner in which a glycerol ester may be caused to provide these products may be seen by considering the nature of the reaction previously cited to illustrate the mode of formation of such esters. From the equation it is seen that the reaction is essentially one of neutralization. The reversal of this reaction, *i.e.*, hydrolysis, should be expected to provide glycerol and an acid.

Fresh fats and oils are nearly odorless and are neutral in reaction. However, if they are exposed to moisture and the action of aerobic bacteria, they are hydrolyzed and are thereupon said to have become *rancid.* The bacterial action usually involves a fermentation or putrefaction of the gelatinous or albuminous substances always found in fats and oils. The usual refining processes render the fats and oils less susceptible to hydrolysis by removing the albuminous constituents.

The distinctly disagreeable odor and taste associated with rancid fats and oils are due to the presence of organic acids produced by hydrolysis. These undesirable properties become apparent even though hydrolysis may have proceeded to only a small extent. Thus, butter becomes unpalatable when even very small quantities of butyric acid are produced by the hydrolysis of glyceryl butyrate.

Manufacture of Soap. In general, the hydrolysis of glyceryl esters occurs only slowly. If, however, these esters are placed in contact with solutions containing high concentrations of hydroxyl ion, the cleavage of the esters occurs rapidly. These conditions may be realized by treating the esters with aqueous solutions of sodium or potassium hydroxides or carbonates at elevated temperatures. This process, which involves the hydrolysis of esters with the aid of alkali, is known as *saponification*, and the products are glycerol and the sodium or potassium salt of the organic acid. The latter is known as *soap.*



Ester (fat or oil) — Glycerol — Soap (sodium salt of organic acid)

Commercially, the reactions employed in the manufacture of soap are carried out in large steam-heated vats. Upon completion of the

saponification, the reaction mixture is a colloidal system in which the soap is the dispersed phase. The soap is coagulated ("salted out") by the addition of an electrolyte, usually sodium chloride. The nature of the fat or oil used in the manufacture of soap varies with the type of soap desired. If a white hard soap is wanted, the best grades of tallow, palm oil, cocoanut oil, or cottonseed oil must be used. The sodium salts of the organic acids derived from the above fats and oils are hard and firm, while the sodium salts of unsaturated acids are soft, like butter. Hard soaps are invariably made with sodium hydroxide or carbonate and with saturated fats and oils. Soft soaps are made from unsaturated oils and usually with potassium hydroxide or carbonate.

35.6. Foods

The organic constituents of the foods consumed by man and other forms of animal life are primarily of interest because of the fact that these materials sustain vital processes. In addition, these same organic forms of matter are important in the sense that they serve as sources of specific organic compounds and as the raw materials for numerous commercial organic processes.

Not all the foods required for an adequate diet are organic. Numerous inorganic compounds (*i.e.*, mineral matter) are essential even though the quantities required may be relatively small. These include compounds of calcium, iron, sodium, potassium, phosphorus, and iodine, as well as water and oxygen.

The numerous and usually somewhat complex organic compounds that make up the bulk of animal foods may be classified into three broad groups, *viz.*, fats, carbohydrates, and proteins. Other essential organic substances include vitamins, enzymes, and hormones, but these are usually required in only very small amounts. As has already been pointed out, fats are glyceryl esters of organic acids, and these esters will not be discussed further as a specific type of compound.

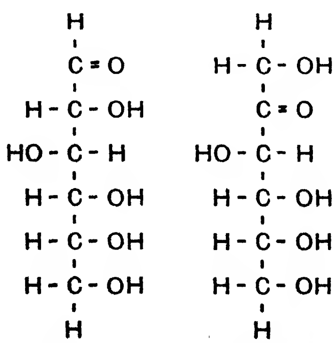
Carbohydrates. The term *carbohydrates* suggests hydrates of carbon, *i.e.*, $C(H_2O)_x$. It is generally true that those compounds designated as carbohydrates consist of carbon in combination with hydrogen and oxygen such that the latter elements are present in the same ratio as in water. Although this basis would include some relatively simple substances such as formaldehyde, the compounds usually thought of as carbohydrates are those containing five or more carbon atoms per molecule. The formulas of most carbohydrates conform to the general formula $(C_6H_{10}O_5)_n(H_2O)_m$, where the numerical value of n is unity or greater and the numerical value of m may be zero, one, or a

number greater than one. Carbohydrates may be classified as mono-, di-, and polysaccharides, depending upon the numerical value of *n* in the general formula given above. A number of typical examples are listed in Table 49.

TABLE 49
SOME COMMON CARBOHYDRATES

Name		Formula
Chemical	Common	
Monosaccharides:		
Glucose	Dextrose or grape sugar	$C_6H_{12}O_6$
Fructose	Levulose or fruit sugar	$C_6H_{12}O_6$
Disaccharides:		
Sucrose	Cane sugar or beet sugar	$C_{12}H_{22}O_{11}$
Lactose	Milk sugar	$C_{12}H_{22}O_{11}$
Maltose	Malt sugar	$C_{12}H_{22}O_{11}$
Polysaccharides:		
Starch	Corn starch or potato starch	$(C_6H_{10}O_5)_x$
Glycogen	Animal starch	$(C_6H_{10}O_5)_y$
Cellulose	Cellulose	$(C_6H_{10}O_5)_z$

In earlier discussions, reference has been made to the fact that many carbohydrate molecules contain the structural groups that are characteristic of the alcohols, the aldehydes, and the ketones. This, together with the formulas listed in Table 49, suggests that carbohydrates must involve rather complex structures involving many possibilities of isomerism. Formulas for the isomeric compounds glucose and fructose are given below. From these formulas it will be evident that both contain —OH groups; glucose is represented as an aldehyde and fructose as a ketone.

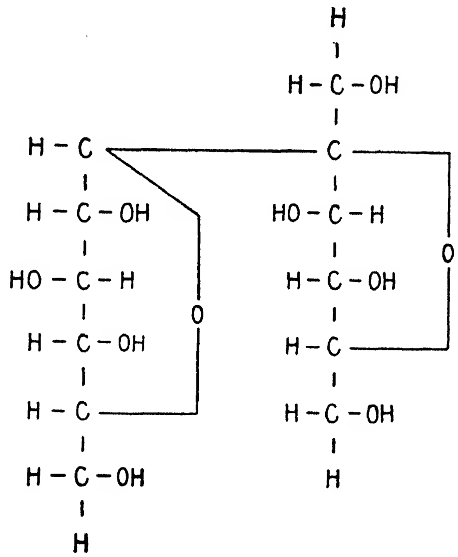


Glucose Fructose

Of the disaccharides, sucrose or ordinary cane sugar is by far the most important. This carbohydrate is readily hydrolyzed under the catalytic influence of acids or enzymes to form the two monosaccharides, glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + HOH \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Although the structural formula of sucrose is not known with certainty, the formula given below is consistent with the fact that sucrose yields glucose and fructose upon hydrolysis and with many other known properties of this substance.



Sucrose

The juices of sugar cane or sugar beets contain 15 to 18 per cent of sucrose. After the juice of sugar cane, for example, is expressed by passing the cane through rollers, the acids present in the juice are neutralized by the addition of lime. The calcium salts of these acids are insoluble and are filtered off with other impurities of a gummy nature. The excess lime is neutralized by addition of carbon dioxide, and the clear juice is then concentrated in evaporators at about 50°C. The resulting sugar is brown and sticky and must be purified by recrystallization. The crude sugar is dissolved in water, and the resulting solution is filtered through boneblack (Sec. 28.3) or other decolorizing carbon beds or filters. Upon concentration of the filtrate, the sugar that crystallizes from the solution is white and very pure.

The polysaccharides are very complex chemical substances. These materials may also be hydrolyzed to form monosaccharides, but the rates of hydrolysis are usually lower than in the case of disaccharides such as sucrose. *Starch* is produced *chiefly* from corn in the United States and from potatoes in European countries. There are available, however, numerous other sources of supply such as rice, wheat, and cassava root (tapioca). *Glycogen* is colloidal in character and is found in muscular tissues and in the liver. The occurrence of glycogen in nature is not restricted to animals since some glycogen is found in plants such as yeast. *Cellulose* is a constituent of the cell walls of most plants. Cotton is one of the most familiar sources of relatively pure cellulose, and wood consists largely of cellulose together with a material known as *lignin.* In the manufacture of paper, the separation of the desired cellulose from the lignin is usually accomplished by a treatment with calcium hydrogen sulfite. The latter converts the lignin to soluble materials from which the cellulose pulp may be separated by filtration. The chief uses for cellulose are in the textile industries and in the manufacture of paper. Esters of cellulose are of major importance in the production of lacquers, plastics, photographic films, etc. Cellulose ethers are used extensively as solvents.

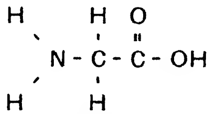
Proteins. The chemical substances known as *proteins* constitute an important class of organic nitrogen compounds found in essentially all types of plant and animal tissue. In addition to carbon, hydrogen, oxygen, and nitrogen, some proteins contain also the elements sulfur, iron, or phosphorus. Most proteins are extremely difficult to purify and may be obtained in a crystalline condition only with difficulty, if at all. That proteins are very complex chemical substances may be inferred from the fact that reasonable estimates of the *molecular weights* of different common proteins are within the range of 18,000 to 300,000.

Much of the presently available information concerning the chemical character of proteins has been obtained through the study of decomposition products of these substances. One property common to all proteins—irrespective of their molecular size or structure—is the fact that they yield *amino acids* upon hydrolysis. These hydrolytic reactions are catalyzed by acids, bases, or enzymes. The structural unit which appears to be characteristic of all proteins is

$$\begin{array}{ccccccc} & & O & & H & & \\ | & & \| & & | & & | \\ -C & - & C & - & N & - & C- \\ | & & & & & & | \end{array}$$

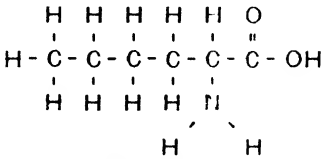
The hydrolysis of any given protein usually results in the formation of

a considerable number of different amino acids. These are organic acids that contain an amino group attached to a carbon atom of the hydrocarbon radical attached to the carboxyl group. The simplest representative is aminoacetic acid or *glycine.*

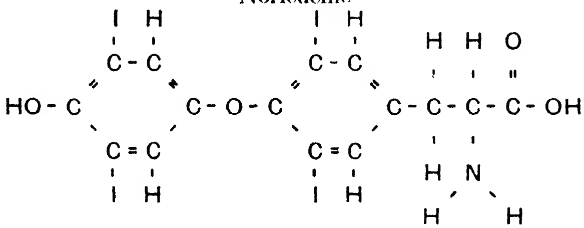


Glycine

Somewhat more complex amino acids are *norleucine*, which is found in the brain, and *thyroxine*, which is a constituent of the thyroid gland.



Norleucine



Thyroxine

In protein molecules, different amino acids are joined together through the characteristic grouping given above and these linkages are ruptured upon hydrolysis. Through the study of the hydrolysis of complex proteins, it has been possible to gain some information as to their chemical character.

Among the proteins of vegetable origin are gliadin, zein, edestin, glutenin, betaine, etc. Proteins of animal origin include egg albumen, casein, keratin, elastin, serum globulin, collagen, etc. Since a detailed knowledge of the structure of protein molecules is lacking, any attempt at classification is bound to be difficult and the results none too satisfactory. The usual classification is that given below.

1. *Simple Proteins.* Among these are the water-soluble egg albumen, the serum globulin of the blood, and edestin from hemp seed (these proteins are soluble in dilute solutions of sodium chloride), the acid- or alkali-soluble glutenin of wheat, the alcohol-soluble gliadin of wheat or zein of corn, and the insoluble keratin found in hair and horn.

2. *Conjugated Proteins.* The protein molecules of the members of this group are joined to other molecules, such as carbohydrates or phosphoric acid. Typical examples are casein from milk and hemoglobin from blood.

3. *Derived Proteins.* These are produced from more complex proteins through hydrolysis catalyzed by the enzyme *pepsin.* These hydrolysis products occupy a position intermediate between the usual proteins and the amino acids. Most of the derived proteins are soluble in water.

Vitamins. In addition to the carbohydrates and proteins, an interesting group of naturally occurring organic compounds recognized as essential constituents of foods is known as the *vitamins.* Although these substances may be present only in relatively small amounts, it has been amply demonstrated that they are essential to proper growth, good health, and in fact to the maintenance of life itself. In present-day society one could scarcely avoid being aware of the existence of these organic compounds. As judged from the overemphasis encountered in modern radio and newspaper advertising, one is tempted to speculate as to how the human race survived up to the time when daily dosages of vitamin pills became available. The answer is, of course, that nature has provided these materials and in most cases one secures adequate supplies by the simple process of consuming a well-balanced diet. However, there are many cases in which diseases related to vitamin deficiencies may be alleviated by the consumption of quantities of vitamins greater than would normally be made available through even an otherwise safe diet.

Practically everyone is familiar with terms such as *vitamin B* and *vitamin C.* In certain cases these designations refer to specific chemical compounds; in other cases (*e.g.*, vitamins A, D, and E) groups of related compounds are involved. In Table 50 some information relative to the natural origin and biological significance of the known vitamins is given. Further information concerning the chemical nature of these substances will be found in Chap. XXXVI.

Enzymes may be looked upon as specific catalysts for biochemical reactions. These substances are proteinlike and yet are not to be classed as typical proteins. Despite their complexity, many enzymes have been isolated in a pure crystalline condition, and much is known concerning their ability to alter the rates of certain reactions. The enzyme *invertase* is produced by yeast and is a catalyst for the hydrolysis of certain di- and polysaccharides. By the action of the enzyme *diastase,* which is produced by sprouting barley, starch is hydrolyzed to monosaccharides and other hydrolysis products. The catalytic

TABLE 50

THE KNOWN VITAMINS

Name	Molecular formula	Prominent occurrence	Symptoms of deficiency
Vitamin A....	Several related compounds exhibit vitamin A activity	Fish-liver oils, egg yolk, butter fat, green and yellow vegetables	Night blindness, temporary sterility in male rats, certain types of infection of epithelial tissue
Vitamin B_1 (thiamin)	$C_{12}H_{18}Cl_2ON_4S$	Milk, green vegetables, rice polishings, yeast, fruits, peanuts	Lack of appetite, retarded growth, beriberi, polyneuritis, low gastric acidity, constipation
Vitamin C (ascorbic acid)	$C_6H_8O_6$	Citrus fruits, tomatoes, leafy green vegetables, potatoes	Symptoms of scurvy, *i.e.*, hemorrhages of skin and gums, palpitation of heart, dental caries, etc.
Vitamin D....	More than one compound is known to possess vitamin D activity	Milk, fish-liver oils, egg yolks, cereals irradiated with ultraviolet light	The disease known as rickets
Vitamin E....	Numerous compounds. α-Tocopherol ($C_{29}H_{50}O_2$) is the most potent	Wheat-germ oil, cottonseed oil, green leafy vegetables	Permanent sterility, muscular lesions
Vitamin K....	Numerous related compounds	Putrefied fish meal, hog-liver fat, alfalfa	Nutritional significance unknown. Useful in treatment of obstructive jaundice, hemorrhages, etc.
	Other vitamins known collectively as Vitamin B		
Riboflavin....	$C_{17}H_{20}O_6N_4$	Beef liver (meats in general), eggs, milk	Lack of growth in young; lesions of the lips, etc., in humans
Nicotinic acid	$C_6H_5O_2N$	Meats, whole wheat, rolled oats, green peas	Symptoms characteristic of pellagra
Pyridoxin (B_6)	$C_8H_{11}O_3N$	Widespread	Dermatitis in rats
Pantothenic acid	$C_9H_{17}O_5N$	Milk, eggs, beef liver, cereals, potatoes, etc.	Dermatitis and failure of growth in young animals; gray hair in animals
Biotin........	$C_{10}H_{16}O_3N_2S$	Widespread. Produced by numerous kinds of bacteria	
Inositol......	$C_6H_{12}O_6$	Occurs generally in animal tissues	Not well known
p-Amino-benzoic acid	$C_7H_7O_2N$	Widespread	

action of enzymes is of importance in alcoholic fermentation. Diastase is employed to convert starch and sugar into monosaccharides which in turn undergo alcoholic fermentation,

$$\underset{\text{Monosaccharide}}{C_6H_{12}O_6} \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_6O} + CO_2$$

brought about by the enzyme known as *zymase.*

Hormones are usually designated as organic substances that act as regulators of bodily functions either by catalysis or some other little-understood mechanisms. Although most of the known hormones are produced within the various glands of the body, some are of vegetable origin and are consumed as components of foods derived from plants. The hormone *secretin* regulates or stimulates the secretion of the pancreas and may influence also the secretion of bile by the liver. Many hormones are recognized, but further discussion of their chemical character or physiological significance is beyond the scope of the present discussion.

The rather evidently heterogeneous character of the topics included in the preceding discussion is not inappropriate. The wide variety of the materials included serves to emphasize the fact that the natural stores of organic substances are widely distributed and diverse in their form of occurrence. By no means all the natural sources of organic compounds have been discussed. Rather an effort has been made only to include a few of the more familiar and important sources.

EXERCISES

1. Given a typical sample of natural gas, suggest methods that might be useful in separating such a mixture into its components.
2. Why is it difficult to obtain pure hydrocarbons from crude petroleum?
3. What determines the order in which the hydrocarbons of petroleum volatilize during distillation?
4. List the more important organic substances obtained by the destructive distillation of (*a*) wood, (*b*) coal.
5. What determines whether a particular fat or oil will be a liquid or a solid under ordinary conditions of temperature?
6. By what simple chemical reaction could one determine whether a particular fat or oil is saturated or unsaturated?
7. What chemical changes are involved in the development of rancidity in fats or oils?
8. List the raw materials required for the manufacture of soft and hard soaps. What important by-product is formed in either case?
9. From the standpoint of the types of organic compounds concerned, what are the essential differences between the three major classes of food?

10. Identify each of the following terms: (*a*) saponification, (*b*) olein, (*c*) hormones, (*d*) pyroligneous acid, (*e*) coal tar, (*f*) enzyme, (*g*) casinghead gasoline, (*h*) disaccharide, (*i*) amino acid, (*j*) conjugated protein.

11. What possible reaction is suggested by the fact that the molecules of amino acids contain both the basic amino group and the acidic carboxyl group?

12. Indicate suitable natural sources of (*a*) vitamin C, (*b*) glycerol, (*c*) linolein, (*d*) acetone, (*e*) fructose, (*f*) vitamin E, (*g*) cellulose.

13. Describe briefly the commercial procedure used in the production of sucrose.

14. If one starts with 1 lb. of a monosaccharide such as glucose and uses the process of alcoholic fermentation, what is the maximum weight (in grams) of ethanol that could be produced? Calculate also the volume of carbon dioxide that would be liberated at 26°C. and 692 mm.

SUGGESTED READING

Journal of Chemical Education

BRUUN, What is Petroleum?, **8,** 1930 (1931).
EGLOFF, Newer Products from Petroleum, **10,** 524 (1933).
WILSON, Foundation and Development of the Gas Industry in America, **18,** 103 (1941).
SNELL, Soap and Glycerol, **19,** 172 (1942).
PRESTON, The Modern Soap Industry, **2,** 1035, 1130 (1925).
MATTILL, The Role of Mineral Salts in Animal Life, **4,** 1269 (1927).
SHANE, On Starch, **14,** 460 (1937).
SCHERER, Cellulose and Its Place in Industry, **10,** 131 (1933).
HERTY, Future Possibilities in the Utilization of Cellulose, **6,** 829 (1929).
FREUDENBERG, The Relation of Cellulose to Lignin in Wood, **9,** 1171 (1932).
FABER, The Development of Protein Chemistry, **15,** 434 (1938).
CARPENTER, Recent Advances in the Chemistry of the Proteins, **18,** 274 (1941).
SHERMAN, The Vitamins, **3,** 1240, 1416 (1926); **4,** 66, 214, 323, 474 (1927).
LEVINE, The Vitamins, **12,** 357, 429 (1935).
ADDINALL, The Vitamins, **19,** 203 (1942).
SHERMAN, Enzymes and Vitamins in Present-day Chemistry, **8,** 652 (1931).
HARROW, Hormones, **8,** 661 (1931).

Industrial and Engineering Chemistry

GUY, Agricultural Uses of Coal and Its Products, **35,** 139 (1943).
KATZEN and OTHMER, Wood Hydrolysis, **34,** 314 (1942).

Book

WILLIAMS, "What to Do about Vitamins," University of Oklahoma Press, Norman, Okla., 1945.

CHAPTER XXXVI

ORGANIC CHEMISTRY

IV. ORGANIC SYNTHETIC PRODUCTS

The simple fact that many and varied organic compounds are obtainable from natural sources does not in any sense imply a limitation upon the number of chemical substances available for the use of mankind. Although it is true that many useful and familiar products are obtained directly from nature, there are many equally useful and important products that probably do not occur naturally. It is literally true that modern chemistry has provided not only many new products but also many that are distinctly superior to similar materials formed by natural processes.

The chemist's ability to duplicate or improve upon nature is by no means limited to the field of organic chemistry. An imposing list of analogous past accomplishments in the field of inorganic chemistry could easily be compiled, and there is reason to believe that still more striking examples will be provided in the future.

In the following discussions, the student will frequently encounter terms such as *synthetic products* and *substitutes*. It should be clearly understood that use of these terms does not imply that the substances so designated are necessarily inferior to related natural products. These terms will be used merely to indicate products of laboratory origin in contrast to those of natural origin.

As a result of the tremendous progress made in the organic chemical laboratories and industries during the past few decades, one is confronted with an abundance of examples of new or improved chemical products. The examples chosen for the present discussion are largely, although not exclusively, related to natural products considered in Chap. XXXV.

36.1. Gasoline

The need for a gasoline that will give superior performance in modern high-compression motors and the increasing demand for a motor fuel of this quality have brought forth new methods for the production of more and better gasoline. Natural gasoline obtained by the fractional distillation of crude petroleum is known as *topped* or *straight-*

run gasoline. This is not desirable as a motor fuel because of the knock produced when such a fuel is used in high-compression motors. There are two ways in which chemists and chemical engineers have devised and produced motor fuels having the required properties.

The quality of straight-run gasoline is much improved by the addition of antiknock agents such as lead tetraethyl [$(C_2H_5)_4Pb$] in quantities usually not exceeding 2 to 3 ml. per gal. of gasoline. Although lead tetraethyl is the best antiknock agent available, its use was at first complicated by the fact that spark plugs and other parts of the motor soon became covered by a coating of elemental lead. This was overcome by the simple expedient of adding to the gasoline small quantities of ethylene dibromide and ethylene dichloride. These compounds ensure volatilization of the lead and its elimination through the exhaust. Thus one solution to the problem of providing better motor fuel was found, but the accomplishment of the desired objective was neither simple nor easy.

Another means of providing superior quality gasoline and gasoline in larger quantities has been found. The long-chain hydrocarbons from petroleum (such as those in the gas-oil fraction) are not suitable for use as a fuel for modern automobiles but can be converted into high-quality motor fuel by the so-called *cracking* process. In this process, the long-chain hydrocarbons are decomposed (cracked) at high temperatures and under the influence of catalysts. This decomposition is accomplished in huge production units, which utilize oil in either the liquid or the vapor state and under a range of suitable pressures. The equations given below represent a gross oversimplification but will serve to give some idea as to the nature of the chemical changes involved.

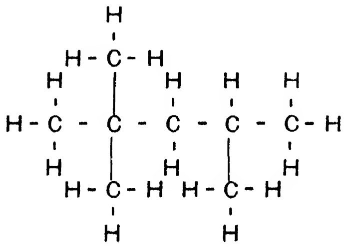
$$C_{14}H_{30} \rightarrow C_8H_{16} + C_6H_{14}$$
$$C_{14}H_{30} \rightarrow C_{11}H_{22} + C_3H_8$$

Actually, the reactions are far more complicated than the simple formation of unsaturated and saturated hydrocarbons indicated above. The carbon chains may break anywhere, *i.e.*, either near one end or farther toward the middle of the chain. Products of the initial decomposition may "crack" to form still shorter carbon chains and ultimately to form some carbon and hydrogen. The unsaturated hydrocarbons also have a tendency to combine with each other to form longer chains. In any case the problem is to adjust conditions so that hydrocarbons (either saturated or unsaturated) of the desired range of molecular weights will be obtained.

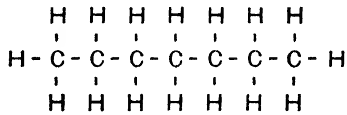
Suitable processing of the crude products of the cracking operation

provides not only gasoline but also many organic chemicals which serve as raw materials for the production of synthetic rubber, chemicals such as ethylene glycol, etc. The utilization of these by-products of the petroleum industry is rapidly becoming one of the most important aspects of the synthetic organic chemicals industry.

Antiknock Rating of Gasolines. The degree to which gasolines possess antiknock properties is expressed in terms of *octane number* or *octane rating*. The hydrocarbon isooctane is used as a basis of comparison and is arbitrarily assigned an antiknock rating of 100. Straight-run gasolines consist largely of straight-chain hydrocarbons and the extent to which such gasoline produces knocking is



iso-Octane



n-Heptane

less than that produced by pure *n*-heptane. Since the antiknock properties of *iso*-octane are superior to those of ordinary gasolines, the antiknock rating of any given gasoline is expressed as the percentage (by volume) of *iso*-octane which must be added to *n*-heptane in order to duplicate the intensity of knocking produced by the gasoline in question. Except for the distinctly inferior grades, most gasolines have an octane number of 70 or above. Gasolines produced by modern catalytic cracking plants, particularly for use in aircraft motors, have octane ratings of about 100 or above.

36.2. Dyes

In Chap. XXXV, it was stated that many organic chemicals obtained from coal tar are used in the manufacture of dyes. These are commonly known as *coal-tar dyes* or *aniline dyes.*

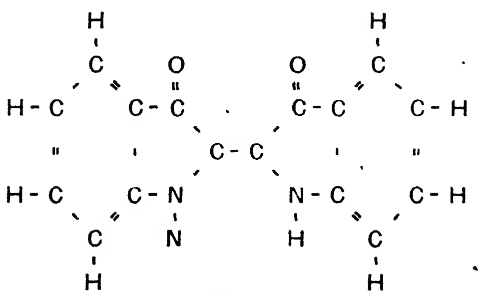
The art of dyeing fabrics and other articles has been practiced for thousands of years. Before the development of the modern dye industries, man had to rely upon coloring matters obtained directly from plants or animals. The scarlet dye cochineal was (and still is) obtained from the insect *Coccus cacti* which is found in Mexico, the Canary Islands, and elsewhere. The ancient Greeks and Romans obtained Tyrian purple from a fluid secreted by certain mollusks. Alizarin or

Turkey red was obtained from the roots of the madder plant, and indigo was produced from various shrubs, called *indigo plants.*

The first synthetic coal-tar dye was accidentally formed during experiments designed to produce quinine. When he was only seventeen years of age, the English chemist, William Henry Perkin (Fig. 147), in 1856 treated aniline with chromic acid and produced the dye known as *mauve.* This discovery quickly led to others and to the establishment of one of the most important of the chemical industries. Prior to the First World War, most coal-tar dyes were produced in Germany. During the war, the United States was cut off from the source of supply, and American chemists were faced with the problem of producing dyestuffs in this country. So well did they succeed that this country was soon in a position not only to supply domestic needs but also to provide dyes for export trade.

Fig. 147.—William Henry Perkin (1838–1907).

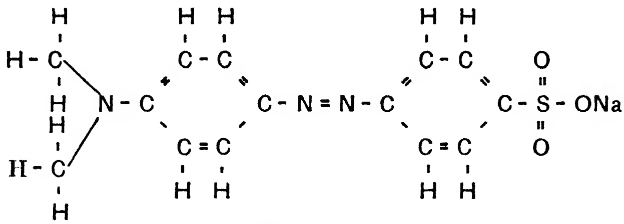
Synthetic dyes are now available to produce almost any conceivable shade of color. These products of the laboratory are purer, more adaptable to a wide variety of dyeing problems, and considerably less expensive than dyes extracted from naturally occurring materials. Most dyes are of complex structure, and the student cannot properly appreciate the chemistry involved in the synthesis of dyes until after a more thorough study of organic chemistry. The structural formula of indigo is given below.



Indigo

The student is already familiar with the use of certain dyes as indicators in neutralization reactions. The dye (indicator) known as

methyl orange may be produced in the laboratory by fairly simple reactions and has the following structure:



Methyl orange

36.3. Synthetic Methanol

The quantity of methyl alcohol that can be produced economically by the destructive distillation of wood is limited. Not only are the supplies of wood to be considered but also the fact that methanol is only one of the products obtained and the quantity of it available from this source is limited by the demand for these other products. For many years it was recognized that much more methyl alcohol could be used to advantage as a radiator antifreeze liquid, in the lacquer and varnish industries, and for many other purposes, if it could be produced synthetically and at lower cost.

During the period 1920 to 1930, methods were discovered and perfected so that methanol could be made from carbon monoxide and hydrogen at less than half its cost from wood. As a result, the production and use of methanol has increased to nearly 20 million gallons annually. The reaction involved,

$$\overline{CO} + 2H_2 \rightarrow CH_4O + \text{heat}$$

is carried out by passing mixtures of carbon monoxide and hydrogen over a solid catalyst (usually copper oxide mixed with oxides of chromium, zinc, vanadium, or manganese) at temperatures from 350° to 600°C. and at pressures from 100 to 200 atm. With proper adjustment of conditions, yields of methanol in excess of 90 per cent may be obtained. Other alcohols are also formed at the same time, and, by proper choice of catalyst, temperature, and pressure, relatively large quantities of these by-products may be obtained. Alcohols that could be produced in this fashion include ethyl, *n*-propyl, isopropyl, and isobutyl alcohols.

The history of the commercial production of methanol is typical of the chemical industries in general. Once cheap and readily available supplies of methanol from inexpensive raw materials have been pro-

vided, corresponding improvements and cost reduction in dependent chemical industries become possible. From the standpoint of the ultimate consumer, it is an encouraging fact that past accomplishments in this direction represent only a beginning.

36.4. Substitutes for Natural Fats

Until comparatively recently, the only fats available for use as foods or other purposes were those of animal origin. By application of some relatively simple chemical information, however, large supplies of animal fat substitutes have been made available. These solid or semisolid products are in no real sense inferior to natural fats and are exemplified by commercial products sold under such trade names as Crisco, Snowdrift, and Spry. In addition, solid products of similar origin are manufactured for use in the production of candles, soaps, waxes, etc.

It has already been pointed out that certain liquid vegetable oils consist, largely, of unsaturated esters (Sec. 35.5). By addition of hydrogen to the double or triple bonds (a process commonly known as *hydrogenation*), these liquid oils may be converted to products that are solid or semisolid depending upon the degree to which the hydrogenation is carried to completion. This hydrogenation invariably requires the use of a catalyst. Although other catalysts are known and may be used to a limited extent, the one most commonly employed is finely divided metallic nickel. The catalyst may be prepared by precipitating nickel hydroxide in the presence of an inert material such as pumice, the particles of which become coated with the precipitate and which therefore acts as a "carrier" for the catalyst. The hydroxide is then reduced to metallic nickel by means of hydrogen at about 300°C. Thereafter, the catalyst is ready for use and need only be protected from contact with the atmosphere in order to avoid oxidation of the extremely finely divided and reactive nickel. The hydrogenation is carried out by agitating the vegetable oil (*e.g.*, cottonseed oil) and catalyst in a closed vessel containing hydrogen gas under a pressure of about 20 lb. per sq. in. and at a temperature of about 200°C.

The physical characteristics of the product depend upon the extent of hydrogenation. If all the double or triple bonds are hydrogenated, the product is hard and waxlike. More commonly, the hydrogenation is stopped at a point such that the product will be a semisolid suitable for use in cooking. The oil is then separated from the catalyst (which may be used again) and allowed to solidify as the temperature is lowered to that of the atmosphere. An important feature of this whole process of hydrogenation is the fact that it requires the use of

very pure hydrogen. Impurities such as hydrogen sulfide and carbon monoxide have a tendency to render the catalyst incapable of performing its function. A catalyst thus affected is said to have been *poisoned.*

36.5. Detergent Soaps

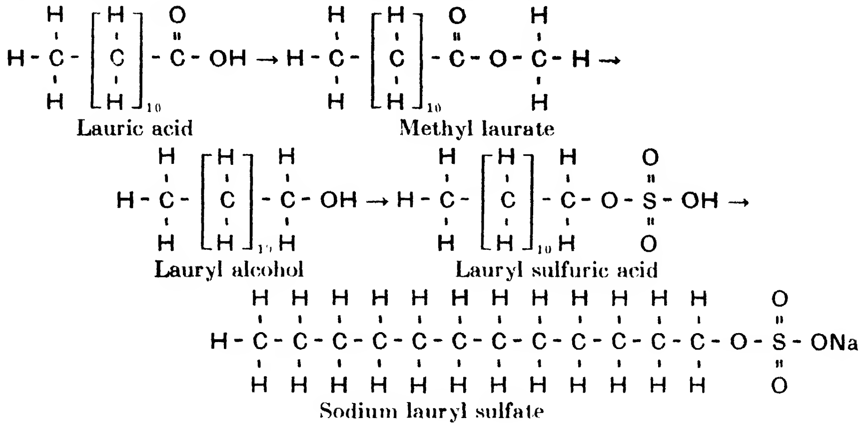
The essential features of the chemistry involved in the manufacture of soap were outlined in Sec. 35.5. Although these procedures provide high-quality products which serve a wide variety of needs, improvements are just as readily possible in this as in any of the other chemical or semichemical industries. These improvements which provide man with new and better chemical products come as the result of deliberate efforts to produce materials having certain desired properties. Although popular books dealing with chemical discoveries tend to overdramatize the accidental, it is more nearly true that most of the important advances in chemical science have come only as the result of much hard work accomplished in spite of many discouraging failures.

In order to appreciate the need for the production of improved types of soap, one need only consider the undesirable properties of ordinary soaps. Because of their tendency to hydrolyze, these soaps are alkaline in reaction and produce a burning sensation when they come into contact with sensitive tissues such as those of the eye. Also because of this alkalinity, the organic acids are often precipitated when one attempts to use ordinary soaps in acidic media. The undesirable precipitation of insoluble curds of "calcium soaps" in hard water has been pointed out previously (Sec. 32.5). Finally, the typical soap products are not soluble in organic solvents and hence are not suitable for use in dry cleaning. In recent years, means of obviating most of these difficulties have been found.

The production of the newer type of detergent soap may be illustrated by the production of sodium lauryl sulfate. By the hydrolysis of the esters present in cocoanut oil, an organic acid known as *lauric acid* is produced. This compound has the following formula:

$$
\begin{array}{cccccccccccccc}
 & H & H & H & H & H & H & H & H & H & H & H & O & \\
 & | & | & | & | & | & | & | & | & | & | & | & \| & \\
H- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & OH \\
 & | & | & | & | & | & | & | & | & | & | & | & & \\
 & H & H & H & H & H & H & H & H & H & H & H & &
\end{array}
$$

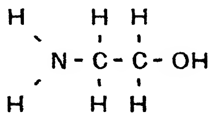
and serves as the starting material. By suitable chemical treatment this acid is successively converted to methyl laurate, lauryl alcohol, lauryl sulfuric acid, and finally to sodium lauryl sulfate. These changes are represented schematically as follows:



Other related compounds may be produced similarly. About the only requirement is that the hydrocarbon part of the molecule should consist of a long straight chain of carbon atoms; usually 10 or more. It should be noted that these "alkyl sulfates" are half esters of an inorganic rather than an organic acid.

These products act as soaps in either hard or soft water and may be used effectively in acid solutions. Furthermore, they are neutral in reaction. The common commercial product known as *Dreft* is an example of a detergent soap.

Another relatively new type of soap is particularly worthy of mention because this type is soluble in certain organic solvents and hence may be used in dry cleaning. These soaps are produced from ethanolamine,



or more directly from the related compounds diethanolamine and triethanolamine. In the form of their sodium salts, these compounds are neutral in reaction and act as soaps in hard or soft water or in some organic solvents. It should be noted that ethanolamine, for example, is both a primary amine and a primary alcohol. This particular compound may be looked upon as one formed by substituting a primary amino group for one of the hydrogen atoms in the molecule of ethyl alcohol.

36.6. Synthetic Vitamins

In the preceding chapter it was indicated that the various vitamins occur in (and therefore may be obtained from) a variety of sources both

animal and vegetable. Although man could depend upon these natural sources for the necessary supplies of vitamins, the advantages inherent in having the pure chemical substances available in large quantities are self-evident. Because of the importance of the vitamins, it seems worth while for the student to gain some idea as to the nature of the tasks that stand between the discovery of a biologically active principle in a natural source and the commercial production of the corresponding pure chemical compound. In considerable measure also, much the same problems must be faced in connection with the identification, synthesis, and production of organic substances other than the vitamins.

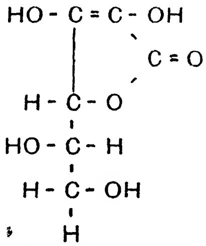
For the purposes of the present discussion, vitamin C is used as an example because this is the one of the best known and, on a weight basis, the most abundant of the water-soluble vitamins. Furthermore, this vitamin is much simpler from the standpoint of chemical constitution than other members of this class of substances.

For at least a hundred years it has been known that fresh fruits contain a material that prevents or cures the disease known as *scurvy*. However, it is only within the past two decades that this material has been known to be identical with the chemical compound now known as vitamin C. When the existence of this material in nature was recognized, the first problem to be solved was that of isolating in pure form the individual compound responsible for the vitamin activity. The choice of the natural source from which isolation of the pure compound is to be attempted is important because this choice largely determines the complexity of the chemical operations required. Initially, the natural material possessing the highest degree of vitamin potency is chosen.

Fresh orange juice contains about 0.05 per cent of vitamin C (by weight). If one wished to isolate 1 g. of the pure vitamin and knew of a chemical process that was nearly perfect, it would be necessary to start with about 5 lb. of the juice. Having concentrated the juice and having separated the bulk of the nonactive components of the solution, the chemist is then in a position to separate and purify the compound in question. Thereafter, there remains the immediate problem of analysis to determine the elemental composition of the pure substance. In the case of vitamin C, the analytical data and molecular weight determinations show that the simplest formula is $C_6H_8O_6$. However, there are many compounds with this same composition, and it is therefore necessary to acquire much more information concerning the chemical characteristics of the compound. It must be learned, for example, whether the molecule contains alcohol, ketone, aldehyde, amino, or

other characteristic groupings. Another useful approach to the study of a substance of unknown structure is that of decomposing the molecule to form two or more simpler molecules which are known or can be more easily identified. If the various "decomposition fragments" can be identified, the chemist may then speculate as to how these fragments may have been joined before decomposition and thus gain some ideas as to the structure of the original molecule. By these and other methods, one may gain a fairly definite idea as to the probable structure of the unknown compound and thus may have a basis for attempts to produce the substance synthetically.

In the case of vitamin C, many years of painstaking work on the part of many chemists finally led to the laboratory synthesis of the compound known as *l-ascorbic* acid.



l-Ascorbic acid
(vitamin C)

The synthetic product proved to possess "vitamin C activity" and to be chemically identical with the vitamin isolated from natural sources. Subsequent to these discoveries, chemical methods were devised for relatively large-scale commercial production of *l*-ascorbic acid, and this vitamin is now available in pure form and in any quantity desired.

Having isolated vitamin C, proved its structure, synthesized it, and provided means for its commercial production, chemists then turned to the synthesis of compounds having similar structures. It is often true that related compounds produced in the laboratory prove to have more pronounced physiological activity than the naturally occurring substance.

Several of the vitamins, as well as a whole host of other naturally occurring substances of biological importance, have been synthesized. These pure substances are now available to the medical profession and are of inestimable value to mankind. It should be recognized, however, that, although much progress has been made in recent years, these accomplishments will undoubtedly be dwarfed by comparison with discoveries that will be made in the future.

36.7. Synthetic Fibers

Until comparatively recently, the only fibers available for use in the manufacture of the common fabrics were the natural fibers, cotton, wool, and silk. Cotton consists almost entirely of cellulose and is the purest form in which cellulose is found in nature. Both silk and wool are nitrogenous substances of considerable complexity and are chemically related to the proteins. When observed under the microscope, silk and cotton appear to have smooth surfaces, while wool fibers present a scaly appearance (Fig. 148).

The high cost of silk early prompted the search for substitutes that would have all the desirable properties of this natural fiber and yet be

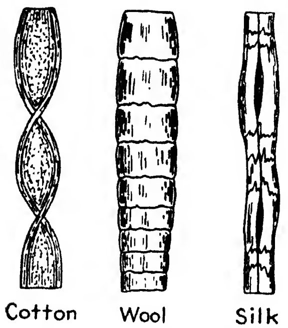


Fig. 148.—The appearance of natural fibers viewed under the microscope.

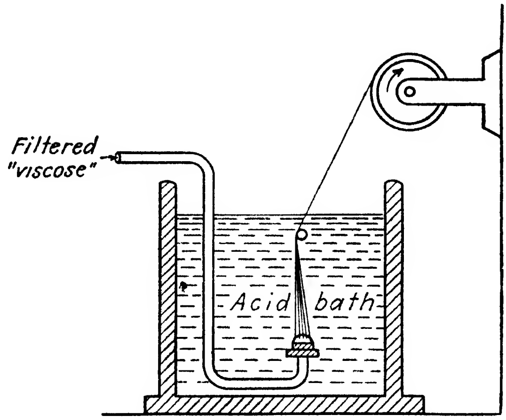


Fig. 149.—The spinning of viscose rayon into threads.

produced at low cost. Although the first artificial silk was probably that produced by the French chemist, de Chardonnet, about 1890, extensive industrial developments in this field have been realized only within the past few years.

Rayon. The raw material for the manufacture of *rayon* is cellulose derived from wood or cotton linters. An important contributing factor in the relatively low cost of rayon is the fact that cotton linters were formerly a waste material for which there were no important uses. The cellulose in these linters (or in wood) is first converted to the sodium salt of cellulose by treatment with sodium hydroxide solution. The sodium cellulose is then converted to cellulose xanthate by treatment with carbon disulfide. In dilute sodium hydroxide, the xanthate exists as a colloidal suspension, known as *viscose.* This colloidal system is passed through a perforated nozzle

(made of a platinum alloy) into a so-called *hardening* bath which contains an aqueous solution of H_2SO_4 and $NaHSO_4$ (Fig. 149). As the viscose emerges in the form of fine streams from the holes in the nozzle or spinneret, the ensuing reaction converts the cellulose xanthate to "regenerated cellulose" filaments, which are subsequently twisted into rayon threads and wound on spools. The size of threads produced is determined by the number and size of the perforations in the spinneret.

In the manufacture of *acetate rayon*, cellulose is converted to cellulose acetate, and this product is aged and dissolved in acetone to form

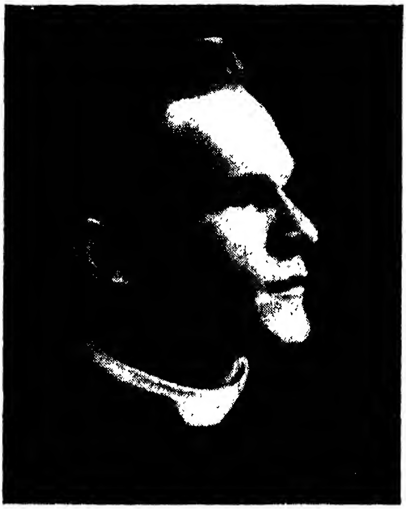


FIG. 150.— Rev. Julius Arthur Nieuwland, C.S.C. (1878–1936). (*Courtesy of The Edgar Fahs Smith Memorial Collection in the History of Chemistry, The University of Pennsylvania.*)

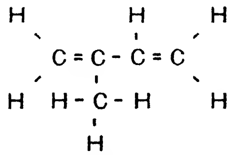
a viscous liquid. This is forced through a spinneret into an atmosphere of moist air whereupon the acetone evaporates and filaments of acetate rayon are formed. *Celanese* is a variety of artificial silk which is made from cellulose acetate in the form of threads having a particularly lustrous appearance.

Nylon. The artificial silk known as *nylon* was developed by the du Pont Company and was first produced commercially in 1940. Nylon is a proteinlike substance formed by the union of certain organic acids containing two carboxyl groups in each molecule and certain amines containing two amino groups in each molecule. The end-to-end union of these two kinds of molecules occurs with elimination of water and the formation of very large chainlike molecules. This product is melted and extruded through spinnerets similar to those used in

the manufacture of rayon. Nylon threads possess greater strength and elasticity than natural silk or any other natural fiber. The use of nylon threads in the fabrication of hosiery, cloth, etc., is familiar to all.

36.8. Synthetic Rubber

Natural rubber is an unsaturated hydrocarbon obtained from a milky fluid known as *latex*, which is produced by certain tropical trees and from a number of other plants. Although natural rubber has been the subject of both chemical and physical investigations for many years, its structure is still unknown. Chemical analysis shows that the simplest formula is C_5H_8, but experiments indicate that rubber has a very high molecular weight. Other lines of investigation show that the simplest structural unit in the rubber molecule is the hydrocarbon known as *isoprene.*

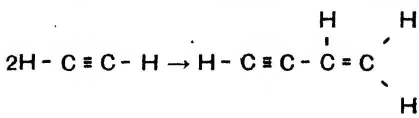


Isoprene

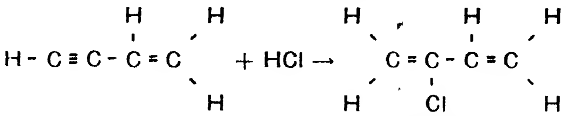
Rubber appears to be a polymerized form of isoprene in which more than a thousand isoprene units are joined end to end to form very long chainlike molecules.

By heating rubber with sulfur (vulcanization) and certain other chemicals, natural rubber may be fabricated into a wide variety of useful forms. However, natural rubber has certain undesirable properties including deterioration upon exposure to sunlight, lack of resistance to attack by acids, oils, organic solvents, etc. These and other factors gave rise to the study of methods for the production of synthetic rubbers.

Neoprene. The development of the synthetic rubber known as *neoprene*, *chloroprene*, or *duprene* has been based upon discoveries made by J. A. Nieuwland (Fig. 150) and his coworkers at Notre Dame University. Their basic discovery consisted in a method whereby gaseous acetylene may be converted to a substance known as *divinylacetylene.* In the laboratories of the du Pont Company, Carothers and others used similar methods to produce monovinylacetylene which was then converted to chloroprene by reaction with hydrogen chloride in the presence of a catalyst consisting of a mixture of ammonium



Monovinylacetylene



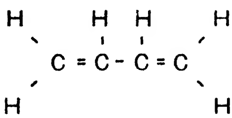
Chloroprene

chloride and cuprous chloride. The polymerization of chloroprene results in the formation of a synthetic rubber which, although more expensive than natural rubber, is superior in many respects. In comparison with natural rubber, neoprene is more resistant toward sunlight, lubricating oils, hydrocarbons, solvents, and acids. Despite the higher cost of production, neoprene has found many applications which take advantage of these properties.

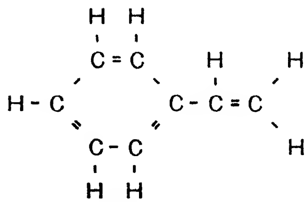
It is of interest to compare chloroprene and isoprene from the standpoint of structural similarity. It is evident that the two differ only in that chloroprene contains Cl in place of the methyl group in the isoprene molecule. The significance of this similarity is borne out by the fact that studies have shown also a marked similarity between the structure of neoprene synthetic rubber and natural rubber.

Buna Rubbers. The unsaturated hydrocarbon *butadiene* and certain of its derivatives were perhaps the first substances used in the production of synthetic rubbers. As early as the First World War, dimethylbutadiene was used in the production of synthetic rubber in Germany. The extensive use of butadiene for such purposes in this country has resulted from the availability of this compound as a product of the "cracking" of petroleum. This is an excellent example of cases in which developments in one chemical industry became possible as a result of advances made in another.

The synthetic rubber known as *Buna* is made by the polymerization of butadiene in the presence of sodium or some other polymerization



Butadiene



Styrene
(phenylethylene)

catalysts. Buna S is a synthetic rubber formed by the copolymerization of butadiene and styrene. A number of other Buna rubbers have been produced by the copolymerization of butadiene and other organic substances.

Thiokol. A somewhat different type of synthetic rubber produced by the Dow Chemical Company is that known as *Thiokol.* This rubber is a highly polymerized form of the product of the interaction of ethylene dichloride and sodium polysulfide (Na_2S_x).

Under the impetus of wartime necessity, the synthetic rubber industry in the United States has expanded at an almost unbelievable rate. It seems evident that large quantities of synthetic rubber will be used in the postwar years for specialized uses and perhaps for general use. This is a natural consequence of the fact that one may produce synthetic rubbers that do not have some of the undesirable properties of natural rubbers. It should also be kept in mind that natural rubber is not likely to be subjected to further improvement, while the possibilities for the discovery of improved synthetic rubbers are practically unlimited.

36.9. Synthetic Resins and Plastics

The polymerization of organic molecules or polymerization following the union of two or more relatively simple organic compounds gives rise to a wide variety of synthetic organic materials commonly referred to as *resins* or *plastics.* By suitable choice of raw materials one may produce resins or plastics having decidedly different properties which render these products adaptable to a veritable multitude of uses. In recent years, resins and plastics have come into use in the form of buttons, brushes, electrical insulators, combs, pencils, gears, dishes, fountain pens, telephone receivers and transmitters, billiard balls, automobile steering wheels, etc., etc. The extent to which resins and plastics now serve as satisfactory substitutes for metals is indeed significant.

Synthetic resins and plastics are characterized by the fact that they can be molded into almost any desired shape. When heated, some of these materials become fluid or semifluid whereupon chemical changes transform the plastics into hard infusible substances. Other resins and plastics may be softened by heat without the occurrence of chemical changes having the result indicated above. In either case, the manufacture of objects made from plastics involves heating followed by molding under pressure. Fillers, such as powdered wood, asbestos, and cotton, as well as coloring matter, may be added depending upon the use for which the final product is intended.

The first synthetic resin to find wide application was that known as *Bakelite* and discovered by the Belgian-American chemist Baekeland. This resin is made by the reaction between formaldehyde and phenol and has been referred to previously (Chap. XXXIV). Other important

synthetic resins and plastics include Lucite (polymerized methyl methacrylate), Styron (polymerized styrene), Plaskon and Beetle (from urea and aldehydes), celluloid (from cellulose nitrate and camphor), etc. The discovery and application of other useful synthetic resins and plastics seem likely to overshadow the not inconsiderable developments in this field during the past few years.

In this, as in other phases of chemistry and its allied sciences, each new fact discovered represents an addition to the accumulation of scientific information. No matter how obscure and unimportant such facts may appear, taken together they lead to a better understanding of the physical world and to new and better products for the use and benefit of mankind.

EXERCISES

1. By means of equations, show at least six possible reactions that might occur during the cracking of the hydrocarbon $C_{12}H_{26}$.

2. Why is ethylene dibromide used as a component of some gasolines?

3. If one wished to control the cracking of a hydrocarbon mixture so as to cause one particular product to predominate, what experimental variables might best be studied in an effort to achieve this objective?

4. Under what conditions might it be possible for a gasoline to have an antiknock rating greater than 100?

5. What factors have an important bearing upon the cost of methanol produced from wood?

6. If carbon can be oxidized to a mixture containing (by weight) 68 per cent CO and 32 per cent CO_2 and if the former can be converted to methanol with an over-all efficiency of 88 per cent, what weight of methanol may be produced from 1.6 tons of carbon?

7. Why must catalysts used in the hydrogenation of oils be protected from exposure to the atmosphere?

8. What properties of detergent soaps make these products superior to ordinary soaps?

9. If vitamins are present in natural products used as foods, why should there be any need to produce synthetic vitamins?

10. What reasons might be given for the high retail cost of synthetic vitamins?

11. Outline the various operations involved in the production of rayon from wood pulp.

12. What simple qualitative test may be used to distinguish between nylon and rayon?

13. From the standpoint of chemical constitution, what property is possessed in common by natural and synthetic rubbers?

14. Explain clearly the meaning of the term polymerization.

15. How do different kinds of resins and plastics behave when subjected to elevated temperatures?

16. What advantages may be cited in connection with the substitution of resins or plastics for metals in the production of (for example) certain parts for automobiles?

SUGGESTED READING

Journal of Chemical Education

THORPE, One Hundred Years of Organic Synthesis, **5,** 1591 (1928).
TORMEY, The Analytical Distillation of Gasoline, **8,** 699 (1931).
WEBB, Dyes and Dyeing, **19,** 460 (1942).
SHREVE, The Dye Industry in America, **3,** 1128 (1926).
DE LONG, Synthetic Methanol—an Accomplishment of Chemical Research, **2,** 429 (1925).
ALMQUIST, Catalytic Synthesis at High Pressures, **3,** 385 (1926).
KREMER, The Ethanolamines, **19,** 80 (1942).
MACK, Textiles and Test Tubes, **6,** 141, 357, 541, 753 (1929).
LUFT, Rayon—Man-made Silk, **2,** 864 (1925).
HUSSEY and SCHERER, Rayon—Today and Tomorrow, **7,** 2543 (1930).
SHOEMAKER, Viscose Rayon, **4,** 1260 (1927).
SHOR, Nylon, **21,** 88 (1944).
KELLY and BRUSON, The Chemistry of Rubber, **3,** 253 (1926).
BRAUER, The Outlook for Synthetic Rubber, **6,** 1286 (1929).
FISHER, Rubber: Newer Theoretical and Practical Developments, **8,** 7 (1931).
OENSLAGER, Recent Developments in the Rubber Industry, **9,** 975 (1932).
FISHER, Natural and Synthetic Rubbers, **19,** 522 (1942).
HAUSER, Synthetic Rubber and Plastics, **21,** 15 (1944).
NEVILLE, Synthetic Resins and Plastics, **19,** 9 (1942).

APPENDIX

I. Units of Measurement

A. Length

1 kilometer = 1000 meters = 0.6214 mile
1 meter = 100 centimeters = 39.37 inches
1 centimeter = 10 millimeters = 0.3937 inch
1 foot = 12 inches = 30.48 centimeters
1 inch = 2.54 centimeters = 25.4 millimeters

B. Volume

1 liter = 1000 milliliters = 1.06 quarts
1 liter = 1000.027 cubic centimeters
1 cubic foot = 28.32 liters = 28,320 cubic centimeters
1 fluid ounce = 29.574 cubic centimeters

C. Weight

1 kilogram = 1000 grams = 2.205 pounds (avoirdupois)
1 pound = 453.592 grams
1 ounce (avoirdupois) = 28.35 grams
1 grain = 0.064799 gram = 64.799 milligrams

D. Temperature

Degrees C. = $\frac{5}{9}$(°F. − 32)
Degrees F. = $\frac{9}{5}$(°C.) + 32
Degrees K. = °C. + 273

II. Vapor Pressure of Water*

Temperature, °C.	Pressure, mm.	Temperature, °C.	Pressure, mm.
0	4.580	31	33.662
5	6.536	32	35.629
10	9.197	33	37.695
15	12.771	34	39.863
16	13.617	35	42.139
17	14.511	36	44.527
18	15.457	40	55.288
19	16.456	45	71.840
20	17.512	50	91.492
21	18.626	55	118.03
22	19.802	60	149.38
23	21.043	65	187.56
24	22.351	70	233.71
25	23.728	75	289.13
26	25.181	80	355.22
27	26.709	85	433.56
28	28.318	90	525.86
29	30.011	95	634.00
30	31.791	100	760.00

* Osborne and Myers, *National Bureau of Standards Journal of Research*, **13**, 11 (1934).

III. pH Range and Color* of Some Common Indicators

Indicator	pH Range and Colors
Methyl violet	*y* 0.15– 3.2 *v*
Thymol blue (acid range)	*r* 1.2 – 2.8 *y*
Methyl orange	*r* 3.1 – 4.4 *y*
Bromphenol blue	*y* 3.0 – 4.6 *p*
Methyl red	*r* 4.2 – 6.3 *y*
Litmus	*r* 4.5 – 8.3 *b*
Bromthymol blue	*y* 6.0 – 7.6 *b*
Phenol red	*y* 6.8 – 8.4 *r*
Thymol blue (basic range)	*y* 8.0 – 9.6 *b*
Phenolphthalein	*c* 8.3 –10.0 *r*
Trinitrobenzene	*c* 12.0 –14.0 *o*

* *o*, orange; *b*, blue; *y*, yellow; *r*, red; *p*, purple; *v*, violet; *c*, colorless.

IV. Physical Properties of Gases

Gas	Freezing temperature, °C.	Boiling temperature,* °C.	Critical temperature, °C.	Critical pressure, atm.
Ammonia	− 77.74	− 33.42	132.4	111.50
Argon	−189.2	−185.9	−122.00	48.0
Carbon dioxide	Sublimes†	− 78.471	31.35	73.0
Carbon monoxide	−207.0	−191.484	−139.00	35.0
Chlorine	−101.6	− 34.6	144.00	76.1
Helium	−269.7	−268.922	−267.9	2.26
Hydrogen	−259.2	−252.780	−239.90	12.8
Neon	−248.7	−245.96	−228.7	25.9
Nitrogen	−210.0	−195.814	−147.10	33.5
Oxygen	−218.4	−182.963	−118.8	49.7
Sulfur dioxide	− 72.7	− 9.989	157.2	77.7

* At pressure of 1 atm.

† Solid carbon dioxide has a vapor pressure of 1 atm. at −78.471°C. and therefore passes directly from the solid state to the gaseous state, *i.e.*, sublimes. If heated under a pressure of 5.3 atm., carbon dioxide melts at −56°C.

V. PHYSICAL PROPERTIES OF THE ELEMENTS*

Element	Symbol	Atomic number	Atomic weight	Physical state†	Density‡	Melting temperature, °C.	Boiling temperature, °C.
Hydrogen	H	1	1.0080	Gas	0.08987	−259 14	−252.7
Helium	He	2	4.003	Gas	0.1785	−269.7	−268.9
Lithium	Li	3	6.940	Solid	0.53	186	>1200
Beryllium	Be	4	9.02	Solid	1.8	1350	(1500)§
Boron	B	5	10.82	Solid	2.5	2300	2550
Carbon	C	6	12.010	Solid	2.26‖	3500	
Nitrogen	N	7	14.008	Gas	1.2506	−209.86	−195.81
Oxygen	O	8	16.000	Gas	1.4290	−218.4	−183.0
Fluorine	F	9	19.00	Gas	1.695	−223	
Neon	Ne	10	20.183	Gas	0.9002	−248.7	−245.9
Sodium	Na	11	22.997	Solid	0.97	97.5	880
Magnesium	Mg	12	24.32	Solid	1.74	651	1110
Aluminum	Al	13	26.97	Solid	2.702	660	1800
Silicon	Si	14	28.06	Solid	2.4	1420	2600
Phosphorus	P	15	30.98	Solid	1.82¶	44.1	
Sulfur	S	16	32.06	Solid	2.07	112.8	
Chlorine	Cl	17	35.457	Gas	3.214	−101.6	−34.6
Argon	A	18	39.944	Gas	1.7824	−189.2	−185.7
Potassium	K	19	39.096	Solid	0.86	62.3	760
Calcium	Ca	20	40.08	Solid	1.55	810	1200
Scandium	Sc	21	45.10	Solid	4.80	220	688
Titanium	Ti	22	47.90	Solid	4.5	1800	3000
Vanadium	V	23	50.95	Solid	5.96	1710	(3000)
Chromium	Cr	24	52.01	Solid	7.1	1615	2200
Manganese	Mn	25	54.93	Solid	7.2	1260	1900
Iron	Fe	26	55.84	Solid	7.86	1535	3000
Cobalt	Co	27	58.94	Solid	8.9	1480	2900
Nickel	Ni	28	58.69	Solid	8.90	1452	2900
Copper	Cu	29	63.57	Solid	8.92	1083	2300
Zinc	Zn	30	65.38	Solid	7.140	419.43	907
Gallium	Ga	31	69.72	Solid	5.91	29.75	>1600
Germanium	Ge	32	72.60	Solid	5.36	958.5	2700
Arsenic	As	33	74.91	Solid	5.7	814	615
Selenium	Se	34	78.96	Solid	4.80	220	688
Bromine	Br	35	79.916	Liquid	3.119	− 7.2	58.78
Krypton	Kr	36	83.7	Gas	3.708	−169	−151.8
Rubidium	Rb	37	85.48	Solid	1.53	38.5	700
Strontium	Sr	38	87.63	Solid	2.6	800	1150
Yttrium	Y	39	88.92	Solid	5.51	1490	(2500)
Zirconium	Zr	40	91.22	Solid	6.4	1700	(>2900)
Columbium	Cb	41	92.91	Solid	8.4	1950	(>3300)
Molybdenum	Mo	42	95.95	Solid	10.2	2625	3700
Ruthenium	Ru	44	101.7	Solid	12.2	2450	(>2700)
Rhodium	Rh	45	102.91	Solid	12.5	1955	(>2500)

V. PHYSICAL PROPERTIES OF THE ELEMENTS.— (*Continued*)

Element	Symbol	Atomic number	Atomic weight	Physical state†	Density‡	Melting temperature, °C.	Boiling temperature, °C.
Palladium	Pd	46	106.7	Solid	12	1555	2200
Silver	Ag	47	107.880	Solid	10.5	960.5	1950
Cadium	Cd	48	112.41	Solid	8.6	320.9	767
Indium	In	49	114.76	Solid	7.3	155	>1450
Tin	Sn	50	118.70	Solid	7.31	231.85	2260
Antimony	Sb	51	121.76	Solid	6.681	630.5	1380
Tellurium	Te	52	127.61	Solid	6.24	452	1390
Iodine	I	53	126.92	Solid	4.93	113.5	184.35
Xenon	Xe	54	131.3	Gas	5.851	−140	−109.1
Cesium	Cs	55	132.91	Solid	1.90	26	670
Barium	Ba	56	137.36	Solid	3.5	850	1140
Lanthanum	La	57	138.92	Solid	6.15	826	1800
Cerium	Ce	58	140.13	Solid	6.90	640	1400
Praseodymium	Pr	59	140.92	Solid	6.5	940	
Neodymium	Nd	60	144.27	Solid	6.9	840	
Samarium	Sm	62	150.43	Solid	7.7	>1300	
Hafnium	Hf	72	178.6	Solid	....	(1700)	(3200)
Tantalum	Ta	73	180.88	Solid	16.6	800	(>4100)
Tungsten	W	74	183.92	Solid	19.3	3370	5900
Rhenium	Re	75	186.31	Solid	21.40	3440	
Osmium	Os	76	190.2	Solid	22.48	2700	(>5300)
Iridium	Ir	77	193.1	Solid	22.4	2350	(>1800)
Platinum	Pt	78	195.23	Solid	21.45	1755	
Gold	Au	79	197.2	Solid	19.3	1063.0	2600
Mercury	Hg	80	200.61	Liquid	13.546	−38.87	356.90
Thallium	Tl	81	204.39	Solid	11.85	303.5	1650
Lead	Pb	82	207.21	Solid	11.34	327.5	16.20
Bismuth	Bi	83	209.00	Solid	9.8	271	1450
Radon	Rn	86	222	Gas	9.73	−71	−61.8
Radium	Ra	88	226.05	Solid	(5)	960	1140
Thorium	Th	90	232.12	Solid	11.2	1845	(>3000)
Uranium	U	92	238.07	Solid	18.7	>1850	

* Most of the data in this table were taken from "Lange's Handbook of Chemistry," Handbook Publishers Inc., Sandusky, Ohio, 1941. Some of the less common elements for which most of the data are not available are omitted.

† Under ordinary atmospheric conditions.

‡ Densities of gases are given in grams per liter at a pressure of 1 atm. Densities of liquids and solids are given in grams per cubic centimeter.

§ Values given in parentheses are estimated.

‖ Graphite.

¶ Yellow phosphorus.

VI. Naturally Occurring Isotopes of the Elements*

Atomic number	Symbol	Number of stable isotopes	Mass numbers in order of decreasing percentage abundance
1	H	2	1 (99.98), 2 (0.02)
2	He	2	4 (100), 3 (trace)
3	Li	2	7 (92.5), 6 (7.5)
4	Be	1	9 (100)
5	B	2	11 (81.6), 10 (18.4)
6	C	2	12 (98.9), 13 (1.1)
7	N	2	14 (99.62), 15 (0.38)
8	O	3	16 (99.76), 18 (0.20), 17 (0.041)
9	F	1	19 (100)
10	Ne	3	20 (90.00), 22 (9.73), 21 (0.27)
11	Na	1	23 (100)
12	Mg	3	24 (77.4), 25 (11.5)
13	Al	1	27 (100)
14	Si	3	28 (89.6), 29 (6.2), 30 (4.2)
15	P	1	31 (100)
16	S	4	32 (95.1), 34 (4.2), 33 (0.74), 36 (0.016)
17	Cl	2	35 (75.4), 37 (24.6)
18	A	3	40 (99.632), 36 (0.307), 38 (0.061)
19	K	3	39 (93.38), 41 (6.61), 40 (0.012)
20	Ca	6	40 (96.96), 44 (2.06), 42 (0.64), 48 (0.19), 43 (0.15), 46 (0.0033)
21	Sc	1	45 (100)
22	Ti	5	48 (73.45), 46 (7.95), 47 (7.75), 49 (5.51), 50 (5.34)
23	V	1	51 (100)
24	Cr	4	52 (83.78), 53 (9.43), 50 (4.49), 54 (2.30)
25	Mn	1	55 (100)
26	Fe	4	56 (91.57), 54 (6.04), 57 (2.11), 58 (0.28)
27	Co	1	59 (100)
28	Ni	5	58 (67.4), 60 (26.7), 62 (3.8), 61 (1.2), 64 (0.88)
29	Cu	2	63 (70.13), 65 (29.87)
30	Zn	5	64 (50.9), 66 (27.3), 68 (17.4), 67 (3.9), 70 (0.5)
31	Ga	2	69 (61.2), 71 (38.8)
32	Ge	5	74 (37.1), 72 (27.3), 70 (21.2), 73 (7.9), 76 (6.5)
33	As	1	75 (100)
34	Se	6	80 (48.0), 78 (24.0), 76 (9.5), 82 (9.3), 77 (8.3), 74 (0.9)
35	Br	2	79 (50.6), 81 (49.4)

* From table of isotopes published by G. T. Seaborg, *Reviews of Modern Physics*, **16**, 1 (1944), which includes also the known artificial radioactive isotopes of the elements.

VI. NATURALLY OCCURRING ISOTOPES OF THE ELEMENTS.—(*Continued*)

Atomic number	Symbol	Number of stable isotopes	Mass numbers in order of decreasing percentage abundance
36	Kr	6	84 (57.11), 86 (17.47), 82 (11.53), 83 (11.53), 80 (2.01), 78 (0.35)
37	Rb	2	85 (72.8), 87 (27.2)
38	Sr	4	88 (82.56), 86 (9.86), 87 (7.02), 84 (0.56)
39	Y	1	89 (100)
40	Zr	5	90 (48), 92 (22), 94 (17), 91 (11.5), 96 (1.5)
41	Cb	1	93 (100)
42	Mo	7	98 (24.1), 96 (16.6), 95 (16.1), 92 (14.9), 97 (9.65), 94 (9.4), 100 (9.25)
44	Ru	7	102 (31.34), 104 (18.27), 101 (16.98), 99 (12.81), 100 (12.70), 96 (5.68), 98 (2.22)
45	Rh	1	103 (100)
46	Pd	6	106 (27.2), 108 (26.8), 105 (22.6), 110 (13.5), 104 (9.3), 102 (0.8)
47	Ag	2	107 (51.9), 109 (48.1)
48	Cd	8	114 (28), 112 (24.2), 111 (13.0), 110 (12.8), 113 (12.3), 116 (7.3), 106 (1.4), 108 (1.0)
49	In	2	115 (95.5), 113 (4.5)
50	Sn	10	120 (28.5), 118 (22.5), 116 (15.5), 119 (9.8), 117 (9.1), 124 (6.8), 122 (5.5), 112 (1.1), 114 (0.8), 115 (0.4)
51	Sb	2	121 (56), 123 (44)
52	Te	8	130 (33.1), 128 (32.8), 126 (19.0), 125 (6.0), 124 (4.5), 122 (2.9), 123 (1.6), 120 (1)
53	I	1	127 (100)
54	Xe	9	132 (26.96), 129 (26.23), 131 (21.17), 134 (10.54), 136 (8.95), 130 (4.07), 128 (1.90), 124 (0.094), 126 (0.088)
55	Cs	1	133 (100)
56	Ba	7	138 (71.66), 137 (11.32), 136 (7.81), 135 (6.59), 134 (2.42), 130 (0.101), 132 (0.097)
57	La	1	139 (100)
58	Ce	4	140 (89), 142 (11), 136 (1), 138 (1)
59	Pr	1	141 (100)
60	Nd	7	142 (25.95), 144 (22.6), 146 (16.50), 143 (13.0), 145 (9.2), 148 (6.8), 150 (5.95)
62	Sm	7	152 (26), 154 (20), 147 (17), 149 (15), 148 (14), 150 (5), 144 (3)

VI. Naturally Occurring Isotopes of the Elements.—(*Continued*)

Atomic number	Symbol	Number of stable isotopes	Mass numbers in order of decreasing percentage abundance
63	Eu	2	153 (50.9), 151 (49.1)
64	Gd	7	158 (23.45), 160 (20.87), 156 (20.59), 157 (16.42), 155 (15.61), 154 (2.86), 152 (0.2)
65	Tb	1	159 (100)
66	Dy	6	164 (28), 163 (24), 162 (24), 161 (22), 160 (1.5), 158 (0.1)
67	Ho	1	165 (100)
68	Er	6	166 (32.9), 168 (26.9), 167 (24.4), 170 (14.2), 164 (1.5), 162 (0.1)
69	Tm	1	169 (100)
70	Yb	7	174 (29.58), 172 (21.49), 173 (17.02), 171 (14.26), 176 (13.38), 170 (4.21), 168 (0.06)
71	Lu	2	175 (97.5), 176 (2.5)
72	Hf	6	180 (35.14), 178 (27.13), 177 (18.47), 179 (13.85), 176 (5.30), 174 (0.18)
73	Ta	1	181 (100)
74	W	5	184 (30.1), 186 (29.8), 182 (22.6), 183 (17.3), 180 (approx. 0.2)
75	Re	2	187 (61.8), 185 (38.2)
76	Os	7	192 (41.0), 190 (26.4), 189 (16.1), 188 (13.3), 187 (1.64), 186 (1.59), 184 (0.018)
77	Ir	2	193 (61.5), 191 (38.5)
78	Pt	5	195 (35.3), 194 (30.2), 196 (26.6), 198 (7.2), 192 (0.8)
79	Au	1	197 (100)
80	Hg	7	202 (29.6), 200 (23.3), 199 (17.0), 201 (13.2), 198 (10.1), 204 (6.7), 196 (0.15)
81	Tl	2	205 (70.9), 203 (29.1)
82	Pb	4	208 (52.3), 206 (23.6), 207 (22.6), 204 (1.5)
83	Bi	1	209 (100)
90	Th	1	232 (100)
92	U	3	238 (99.28), 235 (0.71), 234 (0.006)

VII. Solubility Product Values

Formula	Temperature, °C.	$K_{s.p.}$
Sulfides:		
MnS	18	1.4×10^{-15}
FeS	18	3.7×10^{-19}
ZnS	18	1.2×10^{-23}
NiS	18	1.4×10^{-24}
PbS	18	3.4×10^{-28}
CdS	18	3.6×10^{-29}
CuS	18	8.5×10^{-45}
HgS	18	4×10^{-53}
Chlorides:		
$PbCl_2$	25	1.0×10^{-4}
TlCl	25	2.6×10^{-4}
CuCl	18	1.0×10^{-6}
AgCl	25	1.6×10^{-10}
$HgCl_2$	25	2.6×10^{-15}
HgCl	25	2×10^{-18}
Hydroxides:		
AgOH	20	1.5×10^{-8}
$Mg(OH)_2$	18	1.2×10^{-11}
$Fe(OH)_2$	18	1.6×10^{-14}
$Zn(OH)_2$	20	1.8×10^{-14}
$Mn(OH)_2$	18	4×10^{-14}
$Al(OH)_3$	25	3.7×10^{-15}
$Fe(OH)_3$	18	1.1×10^{-36}
Carbonates:		
$MgCO_3$	12	2.6×10^{-5}
$SrCO_3$	25	1.6×10^{-9}
$BaCO_3$	18	8.1×10^{-9}
$CaCO_3$	25	8.7×10^{-9}
Ag_2CO_3	25	6.2×10^{-12}
$PbCO_3$	18	3.3×10^{-14}
Sulfates:		
Tl_2SO_4	25	3.6×10^{-4}
$CaSO_4$	10	6.1×10^{-5}
$SrSO_4$	17	2.8×10^{-7}
$PbSO_4$	18	1.1×10^{-8}
$BaSO_4$	25	1.1×10^{-10}

VIII. Composition of Alloys*

Composition, %	Trade name	Melting temperature, °C.
Aluminum:		
95 Al, 5 Cu	Lynite, body alloy	650
90 Al, 10 Mg	Magnalium	600
95 Al, 5 Si	Aluminum-silicon 43	577–630
Bismuth:		
52 Bi, 40 Pb, 8 Cd	Eutectic fusible alloy	91.5
50 Bi, 25 Pb, 12.5 Sn, 12.5 Cd	Wood's metal	70–72
Cobalt:		
10–80 Co, 20–35 Cr, 0–25 W, 0.75–2.5 C	Stellite	1150
Copper:		
90 Cu, 10 Al	Aluminum bronze	1050
90 Cu, 9 Al, 1 Fe	Resistac	1066
17 Cu, 33 Au, 20 Ag	8 Carat gold	
61 Cu, 26 Mn, 13 Al	Magnetic alloy	
75 Cu, 25 Ni	Nickel coinage, U.S.A.	
60 Cu, 40 Ni	Constantan	1280
91.6 Cu, 8.25 Sn, 0.15 P	Phosphor bronze 47	
82 Cu, 16 Sn, 2 Zn	Bearing bronze	
90 Cu, 10 Zn	Red brass	1050
67 Cu, 33 Zn	Yellow brass	940
55 Cu, 25 Zn, 20 Ni	Usual German silver	
Gold:		
90 Au, 10 Cu	Coinage gold	940
58 Au, 14–28 Cu, 1–28 Ag	14 Carat gold	
90 Au, 10 Pd	White gold	1265
92 Au, 4.2 Ag, 3.8 Cu	22 Carat gold	
75 Au, 10–20 Ag, 5–15 Cu	18 Carat gold	
Iron:		
98.5 Fe	Wrought iron	1510
80 Fe, 20 Al	Ferro-aluminum	1480
99 Fe, 1 C	Steel	1430
97 Fe, 3 C	White cast iron	1150
94 Fe, 3.5 C, 2.5 Si	Gray cast iron	1230
90–92 Fe, Cr, 0.4 Mn, 0.12 C	Stainless steel	1450
88 Fe, 16–17 Cr, 0.4 Mn, 0.1 C (max.)	Stainless iron	
Fe, 17–20 Cr, 7–10 Ni, 0.5 Mn, 0.5 Si, 0.2 C	Allegheny metal	1430–70
50 Fe, 50 Cr	Ferro-chromium	1460
86 Fe, 13 Mn, 1 C	Manganese steel	1510
96.5 Fe, 3.5 Ni	Nickel steel	1530
95.1 Fe, 3 Ni, 1.5 Cr, 0.4 C	Nickel-chrome steel	
63.8 Fe, 36 Ni, 0.2 C	Invar	1495

* Data from "Lange's Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1941. The alloys are listed alphabetically according to the name of the metal that predominates.

VIII. Composition of Alloys.—(*Continued*)

Composition, %	Trade name	Melting temperature, °C.
97.6 Fe, 2 Si, 0.4 C	Silicon steel	
84.3 Fe, 14.5 Si, 0.85 C, 0.35 Mn	Duriron	1265
94.5 Fe, 5 W, 0.5 C	Tungsten steel	
75 Fe, 18 W, 6 Cr, 0.3 V, 0.7 C	High-speed steel	
Lead:		
99.8 Pb, 0.2 As	Lead for shot	
94 Pb, 6 Sb	Battery plate	300
82 Pb, 15 Sb, 3 Sn	Type metal	
67 Pb, 33 Sn	Plumber's solder	275
50 Pb, 50 Sn	Half-and-half solder	275
Magnesium:		
93.7 Mg, 6 Al, 0.3 Mn	Dowmetal E	610
88 Mg, 12 Al	Dowmetal B	575
85 Mg, 15 Al	Dowmetal C	590
Mercury:		
80 Hg, 20 Bi	Bismuth amalgam	90
70 Hg, 30 Cu	Dentist's amalgam	
Nickel:		
80 Ni, 20 Cr	Chromel A	
60 Ni, 33 Cu, 6.5 Fe	Monel metal	1360
75 Ni, 12 Fe, 11 Cr, 2 Mn	Nichrome wire	
60 Ni, 24 Fe, 16 Cr, 0.1 C	Nichrome	1350
60 Ni, 20 Fe, 20 Mo	Hastelloy A	1300
Platinum:		
80–100 Pt, 0.–20 Rh	Thermocouple rhodium	
Silver:		
90 Ag, 10 Cu	U. S. silver coin	890
63 Ag, 30 Cu, 7.5 Zn	Silver solder	
Tin:		
90 Sn, 10 Sb	Brittania metal	255
90 Sn, 7 Sb, 3 Cu	Babbitt metal	
75 Sn, 12.5 Sb, 12.5 Cu	Antifriction	233
85 Sn, 6.8 Cu, 6 Bi, 1.7 Sb	Pewter	
Tungsten:		
W, 0.5–0.75 ThO_2	Filament tungsten	
Zinc:		
90 Zn, 6 Al, 4 Cu	Aluminum solder	
60 Zn, 40 Cu	White solder	840
63 Zn, 21 Sn, 12 Pb, 3.2 Cu	Battery plate	

IX. Common Names of Chemicals

Common name	Chemical name	Formula
Agate	Silicon dioxide	SiO_2
Alabaster	Calcium sulfate	$CaSO_4 \cdot 2H_2O$
Alum	Potassium aluminum sulfate	$KAl(SO_4)_2 \cdot 12H_2O$
Alundum	Aluminum oxide	Al_2O_3
Aqua ammonia	Ammonium hydroxide	NH_4OH
Aqua fortis	Nitric acid	HNO_3
Aqua regia	Mixture of concentrated HCl and concentrated HNO_3	
Bleaching powder	Calcium chloride hypochlorite	$CaOCl_2$
Blueing	Ferric ferrocyanide	$Fe_4[Fe(CN)_6]_3$
Blue vitriol	Copper sulfate	$CuSO_4 \cdot 5H_2O$
Boracic acid	Boric acid	H_3BO_3
Borax	Sodium tetraborate	$Na_2B_4O_7 \cdot 10H_2O$
Brimstone	Sulfur	S
Burnt alum	Potassium aluminum sulfate	$KAl(SO_4)_2$
Calomel	Mercurous chloride	Hg_2Cl_2
Carbide	Calcium carbide	CaC_2
Caustic potash	Potassium hydroxide	KOH
Caustic soda	Sodium hydroxide	NaOH
Chalk	Calcium carbonate	$CaCO_3$
Chloride of lime	Calcium chloride hypochlorite	$CaOCl_2$
Chrome green	Chromium trioxide	Cr_2O_3
Chrome yellow	Lead chromate	$PbCrO_4$
Copperas	Ferrous sulfate	$FeSO_4 \cdot 7H_2O$
Corrosive sublimate	Mercuric chloride	$HgCl_2$
Fool's gold	Iron disulfide	FeS_2
Flint	Silicon dioxide	SiO_2
Glauber's salt	Sodium sulfate	$Na_2SO_4 \cdot 10H_2O$
Green vitriol	Ferrous sulfate	$FeSO_4 \cdot 7H_2O$
Gypsum	Calcium sulfate	$CaSO_4 \cdot 2H_2O$
Hypo	Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$
Javelle water	Sodium hypochlorite solution	NaOCl
Laughing gas	Nitrous oxide	N_2O
Litharge	Lead monoxide	PbO
Lunar caustic	Silver nitrate	$AgNO_3$
Lye	Sodium hydroxide	NaOH
Marble	Calcium carbonate	$CaCO_3$
Milk of lime	Calcium hydroxide solution	$Ca(OH)_2$
Milk of magnesia	Magnesium hydroxide suspended in water	$Mg(OH)_2$
Muriatic acid	Impure hydrochloric acid	HCl
Niter	Potassium nitrate	KNO_3
Oil of vitriol	Concentrated sulfuric acid	H_2SO_4
Oleum	Fuming sulfuric acid	$H_2SO_4 + SO_3$

IX. Common Names of Chemicals.—(*Continued*)

Common name	Chemical name	Formula
Paris green	Double salt of copper acetate and copper arsenite	$Cu(C_2H_3O_2)_2 \cdot Cu_3(AsO_3)_2$
Peroxide	Hydrogen peroxide solution	H_2O_2
Plaster of Paris	Calcium sulfate	$(CaSO_4)_2 \cdot H_2O$
Potash	Potassium carbonate	K_2CO_3
Prussian blue	Ferric ferrocyanide	$Fe_4[Fe(CN)_6]_3$
Prussic acid	Hydrocyanic acid	HCN
Quicksilver	Mercury	Hg
Red lead	Lead orthoplumbate	Pb_3O_4
Rochelle salt	Potassium sodium tartrate	$KNaC_4H_4O_6$
Rock salt	Sodium chloride	$NaCl$
Rouge	Ferric oxide	Fe_2O_3
Sal ammoniac	Ammonium chloride	NH_4Cl
Sal soda	Sodium carbonate	$Na_2CO_3 \cdot 10H_2O$
Salt cake	Impure sodium sulfate	Na_2SO_4
Saltpeter	Potassium nitrate	KNO_3
Soda ash	Sodium carbonate	Na_2CO_3
Sugar of lead	Lead acetate	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
Turnbull's blue	Ferrous ferricyanide	$Fe_3[Fe(CN)_6]_2$
Verdigris	Basic copper acetate	$Cu(OH)C_2H_3O_2$
Vermilion	Mercuric sulfide	HgS
White arsenic	Arsenious oxide	As_2O_3
White lead	Basic lead carbonate	$Pb_2(OH)_2CO_3$

X. MARKET PRICES OF SOME COMMON CHEMICALS*

Chemical	Quantity	Price
Acetaldehyde	Lb.	$ 0.11
Acetone	Lb.	0.07
Acid acetic, 28%	100 lb.	3.38
Acetic, glacial, 99.5%	100 lb.	9.15
Acetylsalicylic	Lb.	0.45
Formic, 90%	Lb.	0.11
Hydrochloric	100 lb.	1.75
Nitric	100 lb.	5.00
Phosphoric	Lb.	0.11
Sulfuric	100 lb.	1.50
	Ton	16.50
Aluminum, metal, 98–99%	Lb.	0.15
Chloride	Lb.	0.08
Sulfate	100 lb.	1.15
Ammonia, anhydrous	Ton	59.00
Aqueous	Ton	65.00
Ammonium carbonate	Lb.	0.09
Chloride	100 lb.	5.50
Nitrate	100 lb.	4.35
Sulfate	Ton	28.20
Antimony chloride	Lb.	0.17
Oxide	Lb.	0.15
Arsenious oxide	Lb.	0.04
Chloride	Lb.	1.55
Barium carbonate, 99%	Ton	43.00
Chloride	Ton	73.00
Hydroxide	Lb.	0.06
Nitrate	Lb.	0.10
Bismuth, metal	Lb.	1.25
Nitrate	Lb.	1.30
Subnitrate	Lb.	1.20
Bleaching powder	100 lb.	2.50
Boneblack	Lb.	0.09
Borax	Ton	11.50
Bromine	Lb.	0.23
Cadmium, metal	Lb.	0.90
Calcium acetate	100 lb.	3.00
Carbonate	Lb.	0.03
Chloride	Ton	18.50
Calomel	Lb.	2.44
Carbon disulfide	Lb.	0.05
Dioxide, liquid	Lb.	0.06
Tetrachloride	Gal.	0.73
Chlorine, liquid	100 lb.	1.75

* From *Chemical and Engineering News*, 23, 1388 (1945). These prices apply to purchases of large commercial quantities and vary somewhat in relation to the quantities involved.

X. Market Prices of Some Common Chemicals.—(*Continued*)

Chemical	Quantity	Price
Copper, metal (electrolytic)	Lb.	0.12
Chloride	Lb.	0.15
Oxide	Lb.	0.19
Sulfate	100 lb.	5.00
Epsom salt	100 lb.	1.80
Ether, diethyl	Lb.	0.11
Ethyl acetate, 85–90%	Lb.	0.11
Ethylene glycol	Lb.	0.10
Formaldehyde	Lb.	0.03
Glauber's salt	100 lb.	1.05
Hydrogen peroxide	Lb.	0.16
Iodine, resublimed	Lb.	2.00
Iron chloride	Lb.	0.05
Lead acetate	Lb.	0.13
Arsenate	Lb.	0.11
Metal	Lb.	0.07
Oxide (litharge)	Lb.	0.08
White	Lb.	0.08
Magnesium carbonate	Lb.	0.06
Chloride	Ton	32.00
Oxide	Lb.	0.26
Manganese chloride	Lb.	0.15
Dioxide, 85–90%	Ton	74.00
Mercury, metal	76 lb.	1.40
Mercuric chloride	Lb.	2.01
Methanol, synthetic	Gal.	0.31
Naphthalene	100 lb.	3.00
Nitrobenzene	Lb.	0.08
Paradichlorobenzene	Lb.	0.11
Paris green	Lb	0.20
Phenolphthalein	Lb.	0.80
Phosphorus, red	Lb.	0.40
Platinum, metal	Oz.	36.00
Potassium dichromate	Lb.	0.10
Chlorate	Lb.	0.11
Permanganate	Lb.	0.20
Salt cake	Ton	15.00
Saltpeter	100 lb.	8.20
Silica, amorphous, 96%	Ton	17.00
Silver nitrate	Oz.	0.32
Sodium bicarbonate	100 lb.	1.85
Chloride	Ton	15.70
Cyanide, 96–98%	Lb.	0.15
Dichromate	Lb.	0.07
Nitrate	Ton	27.00

X. MARKET PRICES OF SOME COMMON CHEMICALS.—(*Continued*)

Chemical	Quantity	Price
Sodium Silicate	100 lb.	0.80
Sulfate	100 lb.	1.70
Thiosulfate	100 lb.	2.25
Sulfur	Ton	16.00
Sulfur dioxide	Lb.	0.07
Tin, metal	Lb.	0.52
Tungsten, metal	Lb.	2.60
Zinc, metal	Lb.	0.09
Oxide	Lb.	0.07

CORRELATED LIST OF VISUAL AIDS

The following list of visual aids can be used to supplement some of the material in this book. These films can be obtained from the producer or distributor listed with each title. (The addresses of these producers or distributors are listed at the end of the bibliography.) In many cases these films can also be secured through local film libraries or local film distributors. Many universities also have large film libraries from which motion pictures can be borrowed.

The running time (min) and whether it is silent (si) or sound (sd) are listed with each title. All of those not listed as color (C) are black and white. All of the following are 16-mm motion pictures.

In many cases the motion pictures will have an accompanying instructor's manual.

CHAPTER I

Historical Introduction to the Study of Chemistry (EBF 15min si). Shows experiments at the time of Lavoisier and Priestley and the attempts of the alchemists to produce gold.

Chemistry and a Changing World (EBF 11min sd). Gives an over-all impression of the work of the chemist and the importance of chemistry in the modern world.

Science and Agriculture—The Soy Bean (EBF 11min sd). Shows interdependence of agriculture and industry and the role of the research chemist in agriculture.

CHAPTER III

Chemical Reactions (Bra F 20min sd). Explains the composition of an atom, the relationship between nucleus and electrons, and the nature of chemical reactions.

CHAPTER IV

Energy and Its Transformations (EBF 10min sd). Demonstrates the principles of the conservation of energy and the concepts of power and work.

Catalysis (EBF 11min sd). Shows the nature of catalytic action and indicates its importance in many chemical processes.

Chemistry of Combustion (EPS 11min si—sd). A series of chemical experiments in oxidation and combustion.

CHAPTER IV

Fire Making (EBF 15min si). Demonstrates the phenomena of combustion.

CHAPTER V

Molecular Theory of Matter (EBF 11min sd). Shows the scientific procedures necessary to present and illustrate the molecular theory of matter.

Characteristics of Gases (Bra F 11min sd). Gives an explanation of the physical laws dealing with gases.

CHAPTER VI

Crystallization (Bray 20min si). Shows by experiments how crystals are formed and the peculiarities of size and shape.

Characteristics of Liquids (Bra F 11min sd). Properties and forms that liquids assume.

Characteristics of Solids (Bray 11min sd). Some of the fundamental conceptions of nature and the physical laws involved.

CHAPTER XII

Velocity of Chemical Reactions (EBF 11min sd). Good for showing how the velocity of a chemical reaction is affected by the nature of the reacting substance, its concentration and temperature.

CHAPTER XIV

Electrons (EBF 11min sd). A demonstration of Faraday's laws, valence, Millikan's experiment, principles of vacuum tubes, photoelectric cells, reproducing sound on film, and the determination of the electron's mass.

CHAPTER XVII

Electron—An Introduction (USOE 16min sd). Explains the nature of the electron and demonstrates electronic flow by means of animation.

CHAPTER XVIII

Oxidation and Reduction (EBF 11min sd). Shows examples of oxidation and reduction reactions especially with application to industrial processes.

CHAPTER XIX

Colloids (EBF 11min sd). Explains the characteristics of simple suspensions, emulsions, and colloids.

CHAPTER XIX

Colloids (Rolab 30min si). Demonstrates the many common forms of colloids and shows how to produce colloids artificially.

CHAPTER XXI

Electrochemistry (EBF 11min sd). Demonstrates the transforming of chemical energy into electrical energy and the reverse process (electrolysis), and shows the application of these processes in the storage battery, electroplating, electrorefining, and the production of chemicals.

CHAPTER XXII

Aluminum (EBF 15min si). Shows the mining, concentrating, and processing of aluminum. Some of the fabrication methods are also shown.

Aluminum (OWI 9min sd). A story of the manufacture of aluminum from the bauxite ore to a finished fighting plane.

Aluminum—Mine to Metal (Bur. Mines 30min si). Shows the processes of mining, milling, and reducing bauxite ore and the principal uses of aluminum.

Magnesium—Metal from the Sea (Bur. Mines 23min sd). The production of magnesium from sea water and the part that research engineers play in the process.

Chemical Effects of Electricity (EBF 15min si). Gives a brief story of electroplating and the equipment used.

CHAPTER XXIII

Primary Cell (EBF 11min sd). Explains the operation of the dry cell.

CHAPTER XXV

Alloy Steels—A Story of Their Development (Bur. Mines 20min sd). Traces the development of alloy steels, alloy materials used, and the part played by the laboratory scientist in the development of alloy steels.

CHAPTER XXVI

Alchemist in Hollywood (Solow 35min sd). Shows the chemical phase of the motion-picture industry by demonstrating the chemical reactions in the processing of motion-picture films.

From Mine to Consumer—The Story of Anaconda (Am. Brass 30min si). Shows the mining and purifying of copper and the manufacturing of copper alloys.

CHAPTER XXVI

Copper Smelting (Bur. Mines 15min si). Shows the conversion of copper ore and concentrates into metallic copper.

Copper Refining (Bur. Mines 15min si). Shows the conversion of the metallic copper into chemically pure copper.

Mercury (Bra F 11min sd). Laboratory experiments showing its different uses are given.

CHAPTER XXVII

Iron Mining and Manufacturing (BFS 15min si). Open-pit mining and the manufacturing of iron from the blast-furnace operation to the pouring of the castings.

The Making and Shaping of Steel (Bur. Mines 70min si). Is a series of seven reels progressing from the processing of raw materials to the making of steel and production of the various steel products.

Steel—Man's Servant (US Steel 38min C sd). Gives a story of the making of steel.

Stainless Steel (Allegheny 20min sd). The manufacturing properties and uses of stainless steel are shown.

CHAPTER XXVIII

Sulphur (Bur. Mines 20min si—sd). The story of the mining and processing of sulphur is shown.

The Nitrogen Cycle (EBF 15min si). Gives information about the nitrogen cycle and the various sources of nitrogen.

Mining of Sulphur in the Gold Coast (Freeport Sulphur Co. 18min si—sd). Shows the place of sulphur in modern life and the processes used in deep-well mining of sulphur.

Story of Sulphur (Bra F 11min sd). How it is obtained and experiments showing its chemical and commercial uses are shown.

Structural Carbon and Graphite (Nat'l Carbon 32min si). Properties of carbon and graphite and the construction of an all-carbon heat exchanger.

CHAPTER XXIX

Manufacturing Abrasives (Bur. Mines 22min si—sd). Shows the making of carborundum and the use of abrasives in manufacturing.

Plant Food from Coal (By-product Ammonia 39min sd). Traces the history of nitrogen from the coal age to the modern by-product coking plant.

A Romance of Industry (Carborundum 20min sd). Discovery, production, fabrication, and applications of abrasive products.

CHAPTER XXXII

Common Salt (EBF 15min si). Shows physical and chemical properties of salt and the mining and refining processes.

CHAPTER XXXV

Evolution of the Oil Industry (Bur. Mines 60min si). Traces the development of the oil industry and shows the steps in drilling, pumping, refining, and testing of oil.

Oil for Aladdin's Lamp (Shell 29min sd). Describes the development of petroleum production in the research laboratory and the necessity for continued petroleum research.

Oil From the Earth (Shell 20min sd). Shows the methods for locating oil and the drilling and refining processes.

Petroleum and Its Products (Univ. of Wis. 10min sd). Shows the location of the oil fields in the world, methods of drilling, storing, and transporting petroleum.

10,000 Feet Deep (Shell 20min sd). Modern methods in prospecting and drilling for oil.

Petroleum and Its Uses (Bur. Mines 42min sd). Various uses of petroleum.

CHAPTER XXXVI

Chemical Ethyl Alcohol (DeFrenes 15min si). Shows how industrial alcohol is made.

The Fourth Kingdom: The Story of Bakelite Resinoid (YMCA 30min si—sd). Shows some of the basic chemical processes in the production of phenolic resinoid and some of the uses for Bakelite products.

Synthetic Rubber (Bur. Mines 21min sd). Shows the step-by-step processes involved in the transition of chemicals to synthetic rubber.

Freedom Rides on Rubber (YMCA 30min sd). A short history of the development of the synthetic rubber industry.

The Story of Gasoline (Bur. Mines 39min si). Explains oil refining by fractional distillation, cracking, and polymerization processes.

Origin and Synthesis of Plastics Materials (USOE 20min sd).

Masters of Molecules (Texaco 35min C sd). Modern refining of petroleum to produce high-octane fuels.

SOURCES OF FILMS LISTED ABOVE

Allegheny—Allegheny Ludlum Steel Corporation, Oliver Building, Pittsburgh.

Am. Brass—American Brass Company, General Sales Department, Waterbury, Conn.

BFS—Bailey Film Service, 404 North Goodwin Avenue, Urbana, Ill.

Bra F—Brandon Films, Inc., 1600 Broadway, New York 19.

Bray—Bray Pictures Corporation, 729 Seventh Avenue, New York 19.

Bur. Mines—U. S. Department of Interior, Bureau of Mines Experiment Station, 4800 Forbes Street, Pittsburgh, 13.

By-product Ammonia, Education & Research Bureau, 5010 Broad Street, Columbus, Ohio.

Carborundum Company, Niagara Falls, N. Y.

Castle—Castle Films, Inc., RCA Building, Rockefeller Center, New York 20.

DeFrenes & Company, 1909–11 Buttonwood Street, Philadelphia 30.

EBF—Encyclopaedia Britannica Films, Inc., 1841 Broadway, New York 23.

EPS—Edited Pictures System, Inc., 330 West 42nd Street, New York 18.

Freeport Sulphur Company, 1804 American Bank Building, New Orleans, La.

Nat'l Carbon—National Carbon Company, Advertising Department, 30 East 42nd Street, New York 18.

OWI—Office of War Information, Bureau of Motion Pictures, Washington 25, D. C.

Rolab Photo-Science Laboratories, Sandy Hook, Conn.

Shell Oil Company, 50 West 50th Street, New York 20.

Solow—Sidney Paul Solow, c/o Consolidated Film Industries, Hollywood, Calif.

Texaco—Texaco Company, 135 East 42nd Street, New York 18.

US Steel—U. S. Steel Corporation, Advertising Department, 436 Seventh Avenue, Pittsburgh.

USOE—United States Office of Education (Obtainable from Castle Films, Inc.).

Univ. of Wis.—University of Wisconsin, University Extension Division, Bureau of Visual Instruction, Madison, Wis.

YMCA—YMCA Motion Picture Bureau, 347 Madison Avenue, New York 17.

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PHARMACEUTICS